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Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air

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Disclaimer

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems; implementation of Agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency, including the Office of Air and Radiation, the Office of Toxic Substances, and the Office of Enforcement.

Determination of toxic organic compounds in ambient air is a complex task, primarily because of the wide variety of compounds of interest and the lack of standardized sampling and analysis procedures. This methods Compendium has been prepared to provide a standardized format for such analytical procedures. A core set of five methods is presented in the original document. In an effort to update the original Compendium, four specific methods have been developed and published in a supplemental document. In addition to the Compendium and Supplement, five new methods have been prepared for inclusion. With this addition, the Compendium now contains fourteen standardized sampling and analysis procedures. As advancements are made, the current methods may be modified from time to time along with new additions to the Compendium.

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INTRODUCTION

This Compendium has been prepared to provide regional, state, and local environmental regulatory agencies, as well as other interested parties, with specific guidance on the determination of selected toxic organic compounds in ambient air. Recently, a Technical Assistance Document (TAD) was published which provided guidance to such persons (1). Based on the comments received concerning the TAD, the decision was made to begin preparation of a Compendium which would provide specific sampling and analysis procedures, in a standardized format, for selected toxic organic compounds.

The current Compendium consists of fourteen procedures which are considered to be of primary importance in current toxic organic monitoring efforts. Additional methods will be placed in the Compendium from time to time, as such methods become available. The original methods were selected to cover as many compounds as possible (i.e., multiple analyte methods were selected). The additional methods are targeted toward specific compounds, or small groups of compounds which, for various technical reasons, cannot be determined by the more general methods.

Each of the methods writeups is self contained (including pertinent literature citations) and can be used independent of the remaining portions of the Compendium. To the extent possible the American Society for Testing and Materials (ASTM) standardized format has been used, since most potential users are familiar with that format. Each method has been identified with a revision number and date, since modifications to the methods may be required in the future.

Nearly all the methods writeups have some flexibility in the procedure. Consequently, it is the user's responsibility to prepare certain standard operating procedures (SOPs) to be employed in that particular laboratory. Each method indicates those operations for which SOPs are required.

Table 1 summarizes the methods currently in the Compendium. As shown in Table 1 the first three methods are directed toward volatile nonpolar compounds. The user should review the procedures as well as the background material provided in the TAD (1) before deciding which of these methods best meets the requirements of the specific task.

Table 2 presents a partial listing of toxic organic compounds which can be determined using the current set of methods in the Compendium. Additional compounds may be determined by these methods, but the user must carefully evaluate the applicability of the method before use.

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(1) Riggin, R. M., "Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air", EPA-600/4-83-027, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1983.

TABLE 1. BRIEF METHOD DESCRIPTION AND APPLICABILITY

Method Number	Description	Types of Compounds Determined
TO-1	Tenax GC Adsorption and GC/MS Analysis	Volatile, nonpolar organics (e.g., aromatic hydrocarbons, chlorinated hydrocarbons) having boiling points in the range of 80° to 200°C.
TO-2	Carbon Molecular Sieve Adsorption and GC/MS Analysis	Highly volatile, nonpolar organics (e.g., vinyl chloride, vinylidene chloride, benzene, toluene) having boiling points in the range of -15° to +120°C.
TO-3	Cryogenic Trapping and GC/FID or ECD Analysis	Volatile, nonpolar organics having boiling points in the range of -10° to +200°C.
TO-4	High Volume PUF Sampling and GC/ECD Analysis	Organochlorine pesticides and PCBs
TO-5	Dinitrophenylhydrazine Liquid Impinger Sampling and HPLC/UV Analysis	Aldehydes and Ketones
TO-6	High Performance Liquid Chromatography (HPLC)	Phosgene
TO-7	Thermosorb/N Adsorption	N-Nitrosodimethylamine
TO-8	Sodium Hydroxide Liquid Impinger with High Performance Liquid Chromatography	Cresol/Phenol
TO-9	High Volume Polyurethane Foam Sampling with High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS)	Dioxin

TABLE 1. BRIEF METHOD DESCRIPTION AND APPLICABILITY (Continued)

Method Number	Description	Types of Compounds Determined
TO-10	Low Volume Polyurethane Foam (PUF) Sampling With Gas Chromatography/Electron Capture Detector (GC/ECD)	Pesticides
TO-11	Adsorbent Cartridge Followed By High Performance Liquid Chromatography (HPLC) Detection	Formaldehyde
TO-12	Cryogenic Preconcentration and Direct Flame Ionization Detection (PDFID)	Non-Methane Organic Compounds (NMOC)
TO-13	PUF/XAD-2 Adsorption with Gas Chromatography (GC) and High Performance Liquid Chromatography (HPLC) Detection	Polynuclear Aromatic Hydrocarbons (PAHs)
TO-14	SUMMA® Passivated Canister Sampling with Gas Chromatography	Semi-Volatile and Volatile Organic Compounds (SVOC/VOCs)

TABLE 2. METHOD APPLICABILITY TO COMPOUNDS OF PRIMARY INTEREST

Compound	Applicable Method(s)	Comments
Acenaphthene	TO-14	
Acenaphthylene	TO-14	
Acetaldehyde	TO-5, TO-11	Extension of TO-11
Acetone	TO-11	Extension of TO-11
Acrolein	TO-5, TO-11	Extension of TO-11
Acrylonitrile	TO-2, TO-3	TO-3 yields better recovery data than TO-2.
Aldrin	TO-10	
Allyl Chloride	TO-2, TO-3	TO-3 yields better recovery data than TO-2.
Aroclor 1242, 1254 and 1260	TO-10	
Benzaldehyde	TO-5	
Benzene	TO-1, TO-2, TO-3, TO-14	TO-14 yields better recovery data.
Benzyl Chloride	TO-1, TO-3, TO-14	
Benzo(a)anthracene	TO-13	
Benzo(a)pyrene	TO-13	
Benzo(b)fluoranthene	TO-13	
Benzo(e)pyrene	TO-13	
Benzo(g,h,i)perylene	TO-13	
Benzo(k)fluoranthene	TO-13	
Butyraldehyde	TO-11	Extension of TO-11
Captan	TO-10	
Carbon Tetrachloride	TO-1, TO-2, TO-3 TO-14	Breakthrough volume is very low using TO-1.
Chlordane	TO-10	
Chlorobenzene	TO-1, TO-3, TO-14	
Chloroform	TO-1, TO-2, TO-3 TO-14	Breakthrough volume is very low using TO-1
Chloroprene (2-Chloro-1,3-butadiene)	TO-1, TO-3	The applicability of these methods for chloroprene has not been documented.
Chlorothalonil	TO-10	
Chlorpyrifos	TO-10	
Chrysene	TO-13	
Cresol	TO-8	
Crotonaldehyde	TO-11	Extension of TO-11
4,4'-DDE	TO-4	
4,4'-DDT	TO-4	
1,2-Dibromomethane	TO-14	
1,2-Dichlorobenzene	TO-14	
1,3-Dichlorobenzene	TO-14	
1,4-Dichlorobenzene	TO-1, TO-3, TO-14	
1,1-Dichloroethane	TO-14	
1,2-Dichloroethylene	TO-14	

TABLE 2. METHOD APPLICABILITY TO COMPOUNDS OF PRIMARY INTEREST (Continued)

Compound	Applicable Method(s)	Comments
1,2-Dichloropropane	TO-14	
1,3-Dichloropropane	TO-14	
Dichlorovos	TO-10	
Dicofol	TO-10	
Dieldrin	TO-10	
2,5-Dimethylbenzaldehyde	TO-11	Extension of TO-11
Dioxin	TO-9	
Endrin	TO-10	
Endrin Aldehyde	TO-10	
Ethyl Benzene	TO-14	
Ethyl Chloride	TO-14	
Ethylene Dichloride (1,2-Dichloroethane)	TO-1, TO-2, TO-3 TO-14	Breakthrough volume very low using TO-1.
4-Ethyltoluene	TO-14	
Fluoranthene	TO-13	
Fluorene	TO-13	
Folpet	TO-10	
Formaldehyde	TO-5, TO-11	
Freon 11	TO-14	
Freon 12	TO-14	
Freon 113	TO-14	
Freon 114	TO-14	
Heptachlor	TO-10	
Heptachlor Epoxide	TO-10	
Hexachlorobenzene and α-Hexachlorocyclohexane	TO-10 TO-10	
Hexachlorobutadiene	TO-14	
Hexachlorocyclopentadiene	TO-10	
Hexanaldehyde	TO-11	Extension of TO-11
Indeno(1,2,3-cd)pyrene	TO-13	
Isovaleraldehyde	TO-11	Extension of TO-11
Lindane (α-BHC)	TO-10	
Methoxychlor	TO-10	
Methyl Benzene	TO-14	
Methyl Chloride	TO-14	
Methyl Chloroform (1,1,1-Trichloroethane)	TO-1, TO-2, TO-3 TO-14	Breakthrough volume very low using TO-1.
Methylene chloride	TO-2, TO-3, TO-14	
Mexacarbate	TO-10	
Mirex	TO-10	
Naphthalene	TO-13	
Nitrobenzene	TO-1, TO-3	
N-Nitrosodimethylamine	TO-7	
trans-Nonachlor	TO-10	

TABLE 2. METHOD APPLICABILITY TO COMPOUNDS OF PRIMARY INTEREST (Continued)

Compound	Applicable Method(s)	Comments
Non-methane Organic Compounds	TO-12	
Oxychlordane	TO-10	
Pentachlorobenzene	TO-10	
Pentachlorphenol	TO-10	
p,p'- DDE	TO-10	
p,p'- DDT	TO-10	
Perchloroethylene (tetrachloroethylene)	TO-1, (TO-2?), TO-3, TO-14	TO-2 performance has not been documented for this compound.
Phenanthrene	TO-13	
Phenol	TO-8	
Phosgene	TO-6	
Polychlorinated biphenyls (PCBs)	TO-4, TO-9	
Propanal	TO-5	
Propionaldehyde	TO-11	Extension of TO-11
Pyrene	TO-13	
Ronnel	TO-10	
1,2,3,4-Tetrachlorobenzene	TO-10	Using PUF in combination with Tenax® GC solid adsorbent.
1,1,2,2-Tetrachloroethane	TO-14	
o-Tolualdehyde	TO-11	Extension of TO-11
m-Tolualdehyde	TO-11	Extension of TO-11
p-Tolualdehyde	TO-11	Extension of TO-11
Toluene	TO-1, TO-2, TO-3, TO-14	
1,2,3-Trichlorobenzene	TO-10, TO-14	Using PUF in combination with Tenax® GC solid adsorbent.
1,2,4-Trichlorobenzene	TO-14	
1,1,2-Trichloroethane	TO-14	
Trichloroethylene	TO-1, TO-2, TO-3, TO-14	
2,4,5-Trichlorophenol	TO-10	
1,2,4-Trimethylbenzene	TO-14	
1,3,5-Trimethylbenzene	TO-14	
Valeraldehyde	TO-11	Extension of TO-11
Vinyl Benzene	TO-14	
Vinyl Chloride	TO-2, TO-3, TO-14	
Vinyl Trichloride	TO-14	
Vinylidine Chloride (1,1-dichloroethene)	TO-2, TO-3, TO-14	
o,m,p-Xylene	TO-1, TO-3, TO-14	

METHOD T01-1 Revision 1.0
April, 1984

METHOD FOR THE DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR USING TENAX® ADSORPTION AND GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

1. Scope

1.1 The document describes a generalized protocol for collection and determination of certain volatile organic compounds which can be captured on Tenax® GC (poly(2,6-Diphenyl phenylene oxide)) and determined by thermal desorption GC/MS techniques. Specific approaches using these techniques are described in the literature (1-3).

1.2 This protocol is designed to allow some flexibility in order to accommodate procedures currently in use. However, such flexibility also results in placement of considerable responsibility with the user to document that such procedures give acceptable results (i.e. documentation of method performance within each laboratory situation is required). Types of documentation required are described elsewhere in this method.

1.3 Compounds which can be determined by this method are nonpolar organics having boiling points in the range of approximately 80° - 200°C. However, not all compounds falling into this category can be determined. Table 1 gives a listing of compounds for which the method has been used. Other compounds may yield satisfactory results but validation by the individual user is required.

2. Applicable Documents

2.1 ASTM Standards:

D1356	Definitions of Terms Related to Atmospheric Sampling and Analysis.
E355	Recommended Practice for Gas Chromatography Terms and Relationships.

2.3 Other documents:

Existing procedures (1-3).
U.S. EPA Technical Assistance Document (4).

3. Summary of Protocol

3.1 Ambient air is drawn through a cartridge containing ~1-2 grams of Tenax and certain volatile organic compounds are trapped on the resin while highly volatile organic compounds and most inorganic atmospheric constituents pass through the cartridge. The cartridge is then transferred to the laboratory and analyzed.

3.2 For analysis the cartridge is placed in a heated chamber and purged with an inert gas. The inert gas transfers the volatile organic compounds from the cartridge onto a cold trap and subsequently onto the front of the GC column which is held at low temperature (e.g. - 70°C). The GC column temperature is then increased (temperature programmed) and the components eluting from the column are identified and quantified by mass spectrometry. Component identification is normally accomplished, using a library search routine, on the basis of the GC retention time and mass spectral characteristics. Less sophistacated detectors (e.g. electron capture or flame ionization) may be used for certain applications but their suitability for a given application must be verified by the user.

3.3 Due to the complexity of ambient air samples only high resolution (i.e. capillary) GC techniques are considered to be acceptable in this protocol.

4. Significance

4.1 Volatile organic compounds are emitted into the atmosphere from a variety of sources including industrial and commercial facilities, hazardous waste storage facilities, etc. Many of these compounds are toxic; hence knowledge of the levels of such materials in the ambient atmosphere is required in order to determine human health impacts.

4.2 Conventional air monitoring methods (e.g. for workspace monitoring) have relied on carbon adsorption approaches with subsequent solvent desorption. Such techniques allow subsequent injection of only a small portion, typically 1-5% of the sample onto the GC system. However, typical ambient air concentrations of these compounds require a more sensitive approach. The thermal desorption process, wherein the entire sample is introduced into the analytical (GC/MS) system fulfills this need for enhanced sensitivity.

5. Definitions

Definitions used in this document and any user prepared SOPs should be consistent with ASTM D1356(6). All abbreviations and symbols are defined with this document at the point of use.

6. INTERFERENCES

6.1 Only compounds having a similar mass spectrum and GC retention time compared to the compound of interest will interfere in the method. The most commonly encountered interferences are structural isomers.

6.2 Contamination of the Tenax cartridge with the compound(s) of interest is a commonly encountered problem in the method. The user must be extremely careful in the preparation, storage, and handling of the cartridges throughout the entire sampling and analysis process to minimize this problem.

7. Apparatus

7.1 Gas Chromatograph/Mass Spectrometry system - should be capable of subambient temperature programming. Unit mass resolution or better up to 800 amu. Capable of scanning 30-440 amu region every 0.5-1 second. Equipped with data system for instrument control as well as data acquisition, processing and storage.

7.2 Thermal Desorption Unit - Designed to accommodate Tenax cartridges in use. See Figure 2a or b.

7.3 Sampling System - Capable of accurately and precisely drawing an air flow of 10-500 ml/minute through the Tenax cartridge. (See Figure 3a or b.)

7.4 Vacuum oven - connected to water aspirator vacuum supply.

7.5 Stopwatch

7.6 Pyrex disks - for drying Tenax.

7.7 Glass jar - Capped with Teflon-lined screw cap. For storage of purified Tenax.

7.8 Powder funnel - for delivery of Tenax into cartridges.

7.9 Culture tubes - to hold individual glass Tenax cartridges.

7.10 Friction top can (paint can) - to hold clean Tenax cartridges.

7.11 Filter holder - stainless steel or aluminum (to accommodate 1 inch diameter filter). Other sizes may be used if desired. (optional)

7.12 Thermometer - to record ambient temperature.

7.13 Barometer (optional).

7.14 Dilution bottle - Two-liter with septum cap for standards preparation.

7.15 Teflon stirbar - 1 inch long.

7.16 Gas-tight glass syringes with stainless steel needles - 10-500 µl for standard injection onto GC/MS system.

7.17 Liquid microliter syringes - 5.50 µL for injecting neat liquid standards into dilution bottle.

7.18 Oven - 60 ± 5°C for equilibrating dilution flasks.

7.19 Magnetic stirrer.

7.20 Heating mantel.

7.21 Variac

7.22 Soxhlet extraction apparatus and glass thimbles - for purifying Tenax.

7.23 Infrared lamp - for drying Tenax.

7.24 GC column - SE-30 or alternative coating, glass capillary or fused silica.

7.25 Psychrometer - to determine ambient relative humidity. (optional).

8. Reagents and Materials

8.1 Empty Tenax cartridges - glass or stainless steel (See Figure 1a or b).
8.2 Tenax 60/80 mesh (2,6-diphenylphenylene oxide polymer).
8.3 Glasswool - silanized.
8.4 Acetone - Pesticide quality or equivalent.
8.5 Methanol - Pesticide quality, or equivalent.
8.6 Pentane - Pesticide quality or equivalent.
8.7 Helium - Ultra pure, compressed gas. (99.9999%)
8.8 Nitrogen - Ultra pure, compressed gas. (99.9999%)
8.9 Liquid nitrogen.
8.10 Polyester gloves - for handling glass Tenax cartridges.
8.11 Glass Fiber Filter - one inch diameter, to fit in filter holder. (optional)
8.12 Perfluorotributylamine (FC-43).
8.13 Chemical Standards - Neat compounds of interest. Highest purity available.
8.14 Granular activated charcoal - for preventing contamination of Tenax cartridges during storage.

9. Cartridge Construction and Preparation

9.1 Cartridge Design

9.1.1 Several cartridge designs have been reported in the literature (1-3). The most common (1) is shown in Figure 1a. This design minimizes contact of the sample with metal surfaces, which can lead to decomposition in certain cases. However, a disadvantage of this design is the need to rigorously avoid contamination of the outside portion of the cartridge since the entire surface is subjected to the purge gas stream during the desorption porcess.

Clean polyester gloves must be worn at all times when handling such cartridges and exposure of the open cartridge to ambient air must be minimized.

9.1.2 A second common type of design (3) is shown in Figure 1b. While this design uses a metal (stainless steel) construction, it eliminates the need to avoid direct contact with the exterior surface since only the interior of the cartridge is purged.

9.1.3 The thermal desorption module and sampling system must be selected to be compatible with the particular cartridge design chosen. Typical module designs are shown in Figures 2a and b. These designs are suitable for the cartridge designs shown in Figures 1a and 1b, respectively.

9.2 Tenax Purification

9.2.1 Prior to use the Tenax resin is subjected to a series of solvent extraction and thermal treatment steps. The operation should be conducted in an area where levels of volatile organic compounds (other than the extraction solvents used) are minimized.

9.2.2 All glassware used in Tenax purification as well as cartridge materials should be thoroughly cleaned by water rinsing followed by an acetone rinse and dried in an oven at 250°C.

9.2.3 Bulk Tenax is placed in a glass extraction thimble and held in place with a plug of clean glasswool. The resin is then placed in the soxhlet extraction apparatus and extracted sequentially with methanol and then pentane for 16-24 hours (each solvent) at approximately 6 cycles/hour. Glasswool for cartidge preparation should be cleaned in the same manner as Tenax.

9.2.4 The extracted Tenax is immediately placed in an open glass dish and heated under an infrared lamp for two hours in a hood. Care must be exercised to avoid over heating of the Tenax by the infrared lamp. The Tenax is then placed in a vacuum oven (evacuated using a water aspirator) without heating for one hour. An inert gas (helium or nitrogen) purge of 2-3 ml/minute is used to aid in the removal of solvent vapors. The oven temperature is then increased to 110°C, maintaining inert gas flow and held for one hour. The oven temperature control is then shut off and the oven is allowed to cool to room temperature. Prior to opening the oven, the oven is slightly pressurized with nitrogen to prevent contamination with ambient air. The Tenax is removed from the oven and sieved through a 40/60 mesh sieve (acetone rinsed and oven dried) into a clean glass vessel. If the Tenax is not to be used immediately for cartridge preparation it should be stored in a clean glass jar having a Teflon-lined screw cap and placed in a desiccator.

9.3 Cartridge Preparation and Pretreatment

9.3.1 All cartridge materials are pre-cleaned as described in Section 9.2.2. If the glass cartridge design shown in Figure 1a is employed all handling should be conducted wearing polyester gloves.

9.3.2 The cartridge is packed by placing a 0.5-1cm glasswool plug in the base of the cartridge and then filling the cartridge to within approximately 1 cm of the top. A 0.5-1cm glasswool plug is placed in the top of the cartridge.

9.3.3 The cartridges are then thermally conditioned by heating for four hours at 270°C under an inert gas (helium) purge (100 - 200 ml/min).

9.3.4 After the four hour heating period the cartridges are allowed to cool. Cartridges of the type shown in Figure 1a are immediately placed (without cooling) in clean culture tubes having Teflon-lined screw caps with a glasswool cushion at both the top and the bottom. Each tube should be shaken to ensure that the cartridge is held firmly in place. Cartridges of the type shown in Figure 1b are allowed to cool to room temperature under inert gas purge and are then closed with stainless steel plugs.

9.3.5 The cartridges are labeled and placed in a tightly sealed metal can (e.g. paint can or similar friction top container). For cartridges of the type shown in Figure 1a the culture tube, not the cartridge,is labeled.

9.3.6 Cartridges should be used for sampling within 2 weeks after preparation and analyzed within two weeks after sampling. If possible the cartridges should be stored at -20°C in a clean freezer (i.e. no solvent extracts or other sources of volatile organics contained in the freezer).

10. Sampling

10.1 Flow rate and Total Volume Selection

10.1.1 Each compound has a characteristic retention volume (liters of air per gram of adsorbent) which must not be exceeded. Since the retention volume is a function of temperature, and possibly other sampling variables, one must include an adequate margin of safety to ensure good collection efficiency. Some considerations and guidance in this regard are provided in a recent report (5). Approximate breakthrough volumes at 38°C (100°F) in liters/gram of Tenax are provided in Table 1. These retention volume data are supplied only as rough guidance and are subject to considerable variability, depending on cartridge design as well as sampling parameters and atmospheric conditions.

10.1.2 To calculate the maximum total volume of air which can be sampled use the following equation:

$$V_{MAX} = \frac{V_b x W}{1.5}$$

where

V_{MAX} is the calculated maximum total volume in liters.

V_b is the breakthrough volume for the least retained compound of interest (Table 1) in liters per gram of Tenax.

W is the weight of Tenax in the cartridge, in grams.

1.5 is a dimensionless safety factor to allow for variability in atmospheric conditions. This factor is appropriate for temperatures in the range of 25-30°C. If higher temperatures are encountered the factor should be increased (i.e. maximum total volume decreased).

10.1.3 To calculate maximum flow rate use the following equation:

$$Q_{MAX} = \frac{V_{MAX}}{t} \times 1000$$

where

Q_{MAX} is the calculated maximum flow rate in milliliters per minute.

t is the desired sampling time in minutes. Times greater than 24 hours (1440 minutes) generally are unsuitable because the flow rate required is too low to be accurately maintained.

10.1.4 The maximum flow rate Q_{MAX} should yield a linear flow velocity of 50-500 cm/minute. Calculate the linear velocity corresponding to the maximum flow rate using the following equation:

$$B = \frac{Q_{MAX}}{\pi r^2}$$

where

B is the calculated linear flow velocity in centimeters per minute.

r is the internal radius of the cartridge in centimeters.

If B is greater than 500 centimeters per minute either the total sample volume (V_{MAX}) should be reduced or the sample flow rate (Q_{MAX}) should be reduced by increasing the collection time. If B is less than 50 centimeters per minute the sampling rate (Q_{MAX}) should be increased by reducing the sampling time. The total sample value (V_{MAX}) cannot be increased due to component breakthrough.

10.1.4 The flow rate calculated as described above defines the maximum flow rate allowed. In general, one should collect additional samples in parallel, for the same time period but at lower flow rates. This practice yields a measure of quality control and is further discussed in the literature (5). In general, flow rates 2 to 4 fold lower than the maximum flow rate should be employed for the parallel samples. In all cases a constant flow rate should be achieved for each cartridge since accurate integration of the analyte concentration requires that the flow be constant over the sampling period.

10.2 Sample Collection

10.2.1 Collection of an accurately known volume of air is critical to the accuracy of the results. For this reason the use of mass flow controllers, rather than conventional needle valves or orifices is highly recommended, especially at low flow velocities (e.g. less than 100 milliliters/minute). Figure 3a illustrates a sampling system utilizing mass flow controllers. This system readily allows for collection of parallel samples. Figures 3b shows a commercially available system based on needle valve flow controllers.

10.2.2 Prior to sample collection insure that the sampling flow rate has been calibrated over a range including the rate to be used for sampling, with a "dummy" Tenax cartridge in place. Generally calibration is accomplished using a soap bubble flow meter or calibrated wet test meter. The flow calibration device is connected to the flow exit, assuming the entire flow system is sealed. ASTM Method D3686 describes an appropriate calibration scheme, not requiring a sealed flow system downstream of the pump.

10.2.3 The flow rate should be checked before and after each sample collection. If the sampling interval exceeds four hours the flow rate should be checked at an intermediate point during sampling as well. In general, a rotameter should be included, as showed in Figure 3b, to allow observation of the sampling flow rate without disrupting the sampling process.

10.2.4 To collect an air sample the cartridges are removed from the sealed container just prior to initiation of the collection process. If glass cartridges (Figure 1a) are employed they must be handled only with polyester gloves and should not contact any other surfaces.

10.2.5 A particulate filter and holder are placed on the inlet to the cartridges and the exit end of the cartridge is connected to the sampling apparatus. In many sampling situations the use of a filter is not necessary if only the total concentration of a component is desired. Glass cartridges of the type shown in Figure 1a are connected using teflon ferrules and Swagelok (stainless steel or teflon) fittings. Start the pump and record the following parameters on an appropriate data sheet (Figure 4): data, sampling location, time, ambient temperature, barometric pressure, relative humidity, dry gas meter reading (if applicable) flow rate, rotameter reading (if applicable), cartridge number and dry gas meter serial number.

10.2.6 Allow the sampler to operate for the desired time, periodically recording the variables listed above. Check flow rate at the midpoint of the sampling interval if longer than four hours.

At the end of the sampling period record the parameters listed in 10.2.5 and check the flow rate and record the value. If the flows at the beginning and end of the sampling period differ by more than 10% the cartridge should be marked as suspect.

10.2.7 Remove the cartridges (one at a time) and place in the original container (use gloves for glass cartridges). Seal the cartridges or culture tubes in the friction-top can containing a layer of charcoal and package for immediate shipment to the laboratory for analysis. Store cartridges at reduced temperature (e.g. - 20°C) before analysis if possible to maximize storage stability.

10.2.8 Calculate and record the average sample rate for each cartridge according to the following equation:

$$Q_A = \frac{Q_1 + Q_2 + \ldots Q_N}{N}$$

where

Q_A = Average flow rate in ml/minute.

$Q_1, Q_2, \ldots Q_N$ = Flow rates determined at beginning, end, and immediate points during sampling.

N = Number of points averaged.

10.2.9 Calculate and record the total volumetric flow for each cartridge using the following equation:

$$V_m = \frac{T \times Q_A}{1000}$$

where

V_m = Total volume sampled in liters at measured temperature and pressure.

T_2 = Stop time.

T_1 = Start time.

T = Sampling time = $T_2 - T_1$, minutes

10.2.10 The total volume (V_s) at standard conditions, 25°C and 760 mmHg, is calculated from the following equation:

$$V_s = V_m \times \frac{P_A}{760} \times \frac{298}{273 + t_A}$$

where

P_A = Average barometric pressure, mmHg

t_A = Average ambient temperature, °C.

11. GC/MS Analysis

11.1 Instrument Set-up

11.1.1 Considerable variation from one laboratory to another is expected in terms of instrument configuration. Therefore each laboratory must be responsible for verifying that their particular system yields satisfactory results. Section 14 discusses specific performance criteria which should be met.

11.1.2 A block diagram of the typical GC/MS system required for analysis of Tenax cartridges is depicted in Figure 5. The operation of such devices is described in 11.2.4. The thermal desorption module must be designed to accommodate the particular cartridge configuration. Exposure of the sample to metal surfaces should be minimized and only stainless steel, or nickel metal surfaces should be employed.

The volume of tubing and fittings leading from the cartridge to the GC column must be minimized and all areas must be well-swept by helium carrier gas.

11.1.3 The GC column inlet should be capable of being cooled to -70°C and subsequently increased rapidly to approximately 30°C. This can be most readily accomplished using a GC equipped with subambient cooling capability (liquid nitrogen) although other approaches such as manually cooling the inlet of the column in liquid nitrogen may be acceptable.

11.1.4 The specific GC column and temperature program employed will be dependent on the specific compounds of interest. Appropriate conditions are described in the literature (1-3). In general a nonpolar stationary phase (e.g. SE-30, OV-1) temperature programmed from 30°C to 200°C at 8°/minute will be suitable. Fused silica bonded phase columns are preferable to glass columns since they are more rugged and can be inserted directly into the MS ion source, thereby eliminating the need for a GC/MS transfer line.

11.1.5 Capillary column dimensions of 0.3 mm ID and 50 meters long are generally appropriate although shorter lengths may be sufficient in many cases.

11.1.6 Prior to instrument calibration or sample analysis the GC/MS system is assembled as shown in Figure 5. Helium purge flows (through the cartridge) and carrier flow are set at approximately 10 ml/minute and 1-2 ml/minute respectively. If applicable, the injector sweep flow is set at 2-4 ml/minute.

11.1.7 Once the column and other system components are assembled and the various flows established the column temperature is increased to 250°C for approximately four hours (or overnight if desired) to condition the column.

11.1.8 The MS and data system are set according to the manufacturer's instructions. Electron impact ionization (70eV) and an electron multiplier gain of approximately 5 x 10^4 should be employed. Once the entire GC/MS system has been setup the system is calibrated as described in Section 11.2. The user should prepare a detailed standard operating procedure (SOP) describing this process for the particular instrument being used.

11.2 Instrument Calibration

11.2.1 Tuning and mass standarization of the MS system is performed according to manufacturer's instructions and relevant information from the user prepared SOP. Perfluorotributylamine should generally be employed for this purpose. The material is introduced directly into the ion source through a molecular leak. The instrumental parameters (e.g. lens voltages, resolution, etc.) should be adjusted to give the relative ion abundances shown in Table 2 as well as acceptable resolution and peak shape. If these approximate relative abundances cannot be achieved, the ion source may require cleaning according to manufacturer's instructions. In the event that the user's instrument cannot achieve these relative ion abundances, but is otherwise operating properly, the user may adopt another set of relative abundances as performance criteria.

However, these alternate values must be repeatable on a day-to-day basis.

11.2.2 After the mass standarization and tuning process has been completed and the appropriate values entered into the data system the user should then calibrate the entire system by introducing known quantities of the standard components of interest into the system. Three alternate procedures may be employed for the calibration process including 1) direct syringe injection of dilute vapor phase standards, prepared in a dilution bottle, onto the GC column, 2) Injection of dilute vapor phase standards into a carrier gas stream directed through the Tenax cartridge, and 3) introduction of permeation or diffusion tube standards onto a Tenax cartridge. The standards preparation procedures for each of these approaches are described in Section 13. The following paragraphs describe the instrument calibration process for each of these approaches.

11.2.3 If the instrument is to be calibrated by direct injection of a gaseous standard, a standard is prepared in a dilution bottle as described in Section 13.1. The GC column is cooled to -70°C (or, alternately, a portion of the column inlet is manually cooled with liquid nitrogen). The MS and data system is set up for acquisition as described in the relevant user SOP. The ionization filament should be turned off during the initial 2-3 minutes of the run to allow oxygen and other highly volatile components to elute. An appropriate volume (less than 1 ml) of the gaseous standard is injected onto the GC system using an accurately calibrated gas tight syringe.

The system clock is started and the column is maintained at -70°C (or liquid nitrogen inlet cooling) for 2 minutes. The column temperature is rapidly increased to the desired initial temperature (e.g. 30°C). The temperature program is started at a consistent time (e.g. four minutes) after injection. Simultaneously the ionization filament is turned on and data acquisition is initiated. After the last component of interest has eluted acquisiton is terminated and the data is processed as described in Section 11.2.5. The standard injection process is repeated using different standard volumes as desired.

11.2.4 If the system is to be calibrated by analysis of spiked Tenax cartridges a set of cartridges is prepared as described in Sections 13.2 or 13.3. Prior to analysis the cartridges are stored as described in Section 9.3. If glass cartridges (Figure 1a) are employed care must be taken to avoid direct contact, as described earlier. The GC column is cooled to -70°C, the collection loop is immersed in liquid nitrogen and the desorption module is maintained at 250°C. The inlet valve is placed in the desorb mode and the standard cartridge is placed in the desorption module, making certain that no leakage of purge gas occurs. The cartridge is purged for 10 minutes and then the inlet valve is placed in the inject mode and the liquid nitrogen source removed from the collection trap. The GC column is maintained at -70°C for two minutes and subsequent steps are as described in 11.2.3. After the process is complete the cartridge is removed from the desorption module and stored for subsequent use as described in Section 9.3.

11.2.5 Data processing for instrument calibration involves determining retention times, and integrated characteristic ion intensities for each of the compounds of interest. In addition, for at least one chromatographic run, the individual mass spectra should be inspected and compared to reference spectra to ensure proper instrumental performance. Since the steps involved in data processing are highly instrument specific, the user should prepare a SOP describing the process for individual use. Overall performance criteria for instrument calibration are provided in Section 14. If these criteria are not achieved the user should refine the instrumental parameters and/or operating procedures to meet these criteria.

11.3 Sample Analysis

11.3.1 The sample analysis process is identical to that described in Section 11.2.4 for the analysis of standard Tenax cartridges.

11.3.2 Data processing for sample data generally involves 1) qualitatively determining the presence or absence of each component of interest on the basis of a set of characteristic ions and the retention time using a reverse-search software routine, 2) quantification of each identified component by integrating the intensity of a characteristic ion and comparing the value to that of the calibration standard, and 3) tentative identification of other components observed using a forward (library) search software routine. As for other user specific processes, a SOP should be prepared describing the specific operations for each individual laboratory.

12. Calculations

12.1 Calibration Response Factors

12.1.1 Data from calibration standards is used to calculate a response factor for each component of interest. Ideally the process involves analysis of at least three calibration levels of each component during a given day and determination of the response factor (area/nanogram injected) from the linear least squares fit of a plot of nanograms injected versus area (for the characteristic ion). In general quantities of component greater than 1000 nanograms should not be injected because of column overloading and/or MS response nonlinearity.

12.1.2 In practice the daily routine may not always allow analysis of three such calibration standards. In this situation calibration data from consecutive days may be pooled to yield a response factor, provided that analysis of replicate standards of the same concentration are shown to agree within 20% on the consecutive days. One standard concentration, near the midpoint of the analytical range of interest, should be chosen for injection every day to determine day-to-day response reproducibility.

12.1.3 If substantial nonlinearity is present in the calibration curve a nonlinear least squares fit (e.g. quadratic) should be employed. This process involves fitting the data to the following equation:

$$Y = A + BX + CX^2$$

where

Y = peak area

X = quantity of component, nanograms

A, B, and C are coefficients in the equation

12.2 Analyte Concentrations

12.2.1 Analyte quantities on a sample cartridge are calculated from the following equation:

$$Y_A = A + BX_A + CX_A$$

where

Y_A is the area of the analyte characteristic ion for the sample cartridge.

X_A is the calculated quantity of analyte on the sample cartridge, in nanograms.

A,B, and C are the coefficients calculated from the calibration curve described in Section 12.1.3.

12.2.2 If instrumental response is essentially linear over the concentration range of interest a linear equation (C=0 in the equation above) can be employed.

12.2.3 Concentration of analyte in the original air sample is calculated from the following equation:

$$C_A = \frac{X_A}{V_S}$$

where

C_A is the calculated concentration of analyte in nanograms per liter.

V_S and X_A are as previously defined in Section 10.2.10 and 12.2.1, respectively.

13. Standard Preparation

13.1 Direct Injection

13.1.1 This process involves preparation of a dilution bottle containing the desired concentrations of compounds of interest for direct injection onto the GC/MS system.

13.1.2 Fifteen three-millimeter diameter glass beads and a one-inch Teflon stirbar are placed in a clean two-liter glass septum capped bottle and the exact volume is determined by weighing the bottle before and after filling with deionized water. The bottle is then rinsed with acetone and dried at 200°C.

13.1.3 The amount of each standard to be injected into the vessel is calculated from the desired injection quantity and volume using the following equation:

$$W_T = \frac{W_L}{V_I} x\ V_B$$

where

W_T is the total quantity of analyte to be injected into the bottle in milligrams

W_I is the desired weight of analyte to be injected onto the GC/MS system or spiked cartridge in nanograms

V_I is the desired GC/MS or cartridge injection volume (should not exceed 500) in microliters.

V_B is total volume of dilution bottle determined in 13.1.1, in liters.

13.1.4 The volume of the neat standard to be injected into the dilution bottle is determined using the following equation:

$$V_T = \frac{W_T}{d}$$

where

V_T is the total volume of neat liquid to be injected in microliters.

d is the density of the neat standard in grams per milliliter.

13.1.6 The bottle is placed in a 60°C oven for at least 30 minutes prior to removal of a vapor phase standard.

13.1.7 To withdraw a standard for GC/MS injection the bottle is removed from the oven and stirred for 10-15 seconds. A suitable gas-tight microber syring warmed to 60°C, is inserted through the septum cap and pumped three times slowly. The appropriate volume of sample (approximately 25% larger than the desired injection volume) is drawn into the syringe and the volume is adjusted to the exact value desired and then immediately injected over a 5-10 seconds period onto the GC/MS system as described in Section 11.2.3.

13.2 Preparation of Spiked Cartridges by Vapor Phase Injection

13.2.1 This process involves preparation of a dilution bottle containing the desired concentrations of the compound(s) of interest as described in 13.1 and injecting the desired volume of vapor into a flowing inert gas stream directed through a clean Tenax cartridge.

13.2.2 A helium purge system is assembled wherein the helium flow 20-30 mL/minute is passed through a stainless steel Tee fitted with a septum injector. The clean Tenax cartridge is connected downstream of the tee using appropriate Swagelok fittings. Once the cartridge is placed in the flowing gas stream the appropriate volume vapor standard, in the dilution bottle, is injected through the septum as described in 13.1.6. The syringe is flushed several times by alternately filling the syringe with carrier gas and displacing the contents into the flow stream, without removing the syringe from the septum. Carrier flow is maintain through the cartridge for approximately 5 minutes after injection.

13.3 Preparation of Spiked Traps Using Permeation or Diffusion tubes

13.3.1 A flowing stream of inert gas containing known amounts of each compound of interest is generated according to ASTM Method D3609(6). Note that a method of accuracy maintaining temperature within ± 0.1°C is required and the system generally must be equilibrated for at least 48 hours before use.

13.3.2 An accurately known volume of the standard gas stream (usually 0.1-1 liter) is drawn through a clean Tenax cartridge using the sampling system described in Section 10.2.1, or a similar system. However, if mass flow controllers are employed they must be calibrated for the carrier gas used in Section 13.3.1 (usually nitrogen). Use of air as the carrier gas for permeation systems is not recommended, unless the compounds of interest are known to be highly stable in air.

13.3.3 The spiked cartridges are then stored or immediately analyzed as in Section 11.2.4.

14. Performance Criteria and Quality Assurance

This section summarizes quality assurance (QA) measures and provides guidance concerning performance criteria which should be achieved within each laboratory. In many cases the specific QA procedures have been described within the appropriate section describing the particular activity (e.g. parallel sampling).

14.1 Standard Opreating Procedures (SOPs)

14.1.1 Each user should generate SOPs describing the following activities as they are performed in their laboratory:

1) assembly, calibration, and operation of the sampling system,
2) preparation, handling and storage of Tenax cartridges,
3) assembly and operation of GC/MS system including the thermal desorption apparatus and data system, and
4) all aspects of data recording and processing.

14.1.2 SOPs should provide specific stepwise instructions and should be readily available to, and understood by the laboratory personnel conducting the work.

14.2 Tenax Cartridge Preparation

14.2.1 Each batch of Tenax cartridges prepared (as described in Section 9) should be checked for contamination by analyzing one cartridge immediately after preparation. While analysis can be accomplished by GC/MS, many laboratories may chose to use GC/FID due to logistical and cost considerations.

14.2.2 Analysis by GC/FID is accomplished as described for GC/MS (Section 11) except for use of FID detection.

14.2.3 While acceptance criteria can vary depending on the components of interest, at a minimum the clean cartridge should be demonstrated to contain less than one fourth of the minimum level of interest for each component. For most compounds the blank level should be less than 10 nanograms per cartridge in order to be acceptable. More rigid criteria may be adopted, if necessary, within a specific laboratory. If a cartridge does not meet these acceptance criteria the entire lot should be rejected.

14.3 Sample Collection

14.3.1 During each sampling event at least one clean cartridge will accompany the samples to the field and back to the laboratory, without being used for sampling, to serve as a field blank. The average amount of material found on the field blank cartridge may be subtracted from the amount found on the actual samples. However, if the blank level is greater than 25% of the sample amount, data for that component must be identified as suspect.

14.3.2 During each sampling event at least one set of parallel samples (two or more samples collected simultaneously) will be collected, preferably at different flow rates as described in Section 10.1. If agreement between parallel samples is not generally within ± 25% the user should collect parallel samples on a much more frequent basis (perhaps for all sampling points). If a trend of lower apparent concentrations with increasing flow rate is observed for a set of parallel samples one should consider using a reduced flow rate and longer sampling interval if possible. If this practice does not improve the reproducibility further evaluation of the method performance for the compound of interest may be required.

14.3.3 Backup cartridges (two cartridges in series) should be collected with each sampling event. Backup cartridges should contain less than 20% of the amount of components of interest found in the front cartridges, or be equivalent to the blank cartridge level, whichever is greater. The frequency of use of backup cartridges should be increased if increased flow rate is shown to yield reduced component levels for parallel sampling. This practice will help to identify problems arising from breakthrough of the component of interest during sampling.

14.4 GC/MS Analysis

14.4.1 Performance criteria for MS tuning and mass calibration have been discussed in Section 11.2 and Table 2. Additional criteria may be used by the laboratory if desired. The following sections provide performance guidance and suggested criteria for determining the acceptability of the GC/MS system.

14.4.2 Chromatographic efficiency should be evaluated using spiked Tenax cartridges since this practice tests the entire system. In general a reference compound such as perfluorotoluene should be spiked onto a cartridge at the 100 nanogram level as described in Section 13.2 or 13.3. The cartridge is then analyzed by GC/MS as described in Section 11.4. The perfluorotoluene (or other reference compound) peak is then plotted on an expanded time scale so that its width at 10% of the peak can be calculated, as shown in Figure 6. The width of the peak at 10% height should not exceed 10 seconds. More stringent criteria may be required for certain applications. The assymmetry factor (See Figure 6) should be between 0.8 and 2.0. The assymmetry factor for any polar or reactive compounds should be determined using the process described above. If peaks are observed that exceed the peak width or assymmetry factor criteria above, one should inspect the entire system to determine if unswept zones or cold spots are present in any of the fittings and is necessary. Some laboratories may chose to evaluate column performance separately by direct injection of a test mixture onto the GC column. Suitable schemes for column evaluation have been reported in the literature (7). Such schemes cannot be conducted by placing the substances onto Tenax because many of the compounds (e.g. acids, bases, alcohols) contained in the test mix are not retained, or degrade, on Tenax.

14.4.3 The system detection limit for each component is calculated from the data obtained for calibration standards. The detection limit is defined as

$$DL = A + 3.3S$$

where

DL is the calculated detection limit in nanograms injected.

A is the intercept calculated in Section 12.1.1 or 12.1.3.

S is the standard deviation of replicate determinations of the lowest level standard (at least three such determinations are required.

In general the detection limit should be 20 nanograms or less and for many applications detection limits of 1-5 nanograms may be required. The lowest level standard should yield a signal to noise ratio, from the total ion current response, of approximately 5.

14.4.4 The relative standard deviation for replicate analyses of cartridges spiked at approximately 10 times the detection limit should be 20% or less. Day to day relative standard deviation should be 25% or less.

14.4.5 A useful performance evaluation step is the use of an internal standard to track system performance. This is accomplished by spiking each cartridge, including blank, sample, and calibration cartridges with approximately 100 nanograms of a compound not generally present in ambient air (e.g. perfluorotoluene). The integrated ion intensity for this compound helps to identify problems with a specific sample. In general the user should calculate the standard deviation of the internal standard response for a given set of samples analyzed under identical tuning and calibration conditions. Any sample giving a value greater than ± 2 standard deviations from the mean (calculated excluding that particular sample) should be identified as suspect. Any marked change in internal standard response may indicate a need for instrument recalibration.

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6. Annual Book of ASTM Standards, Part 11.03, "Atmospheric Analysis", American Society for Testing and Material, Philadelphia, Pennsylvania.

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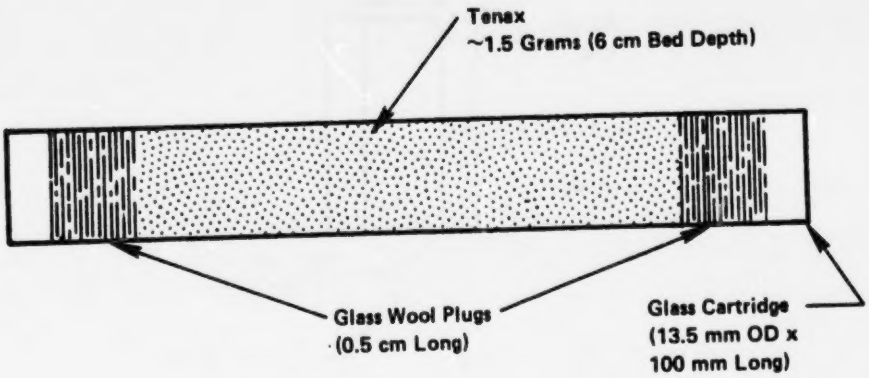
TABLE 1. RETENTION VOLUME ESTIMATES FOR COMPOUNDS ON TENAX

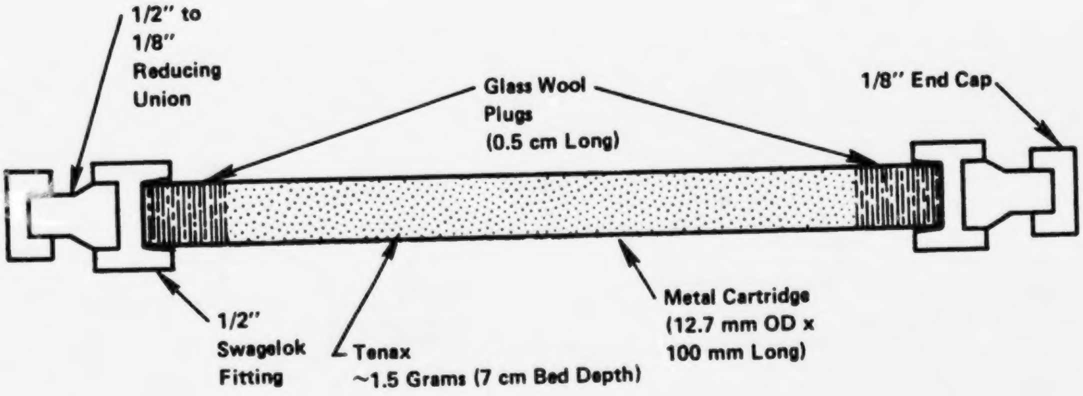
COMPOUND	ESTIMATED RETENTION VOLUME AT 100°F (38°C)-LITERS/GRAM
Benzene	19
Toluene	97
Ethyl Benzene	200
Xylene(s)	~ 200
Cumene	440
n-Heptane	20
1-Heptene	40
Chloroform	8
Carbon Tetrachloride	8
1,2-Dichloroethane	10
1,1,1-Trichloroethane	6
Tetrachloroethylene	80
Trichloroethylene	20
1,2-Dichloropropane	30
1,3-Dichloropropane	90
Chlorobenzene	150
Bromoform	100
Ethylene Dibromide	60
Bromobenzene	300

TABLE 2. SUGGESTED PERFORMANCE CRITERIA FOR RELATIVE ION ABUNDANCES FROM FC-43 MASS CALIBRATION

M/E	% RELATIVE ABUNDANCE
51	1.8 ± 0.5
69	100
100	12.0 ± 1.5
119	12.0 ± 1.5
131	35.0 ± 3.5
169	3.0 ± 0.4
219	24.0 ± 2.5
264	3.7 ± 0.4
314	0.25 ± 0.1

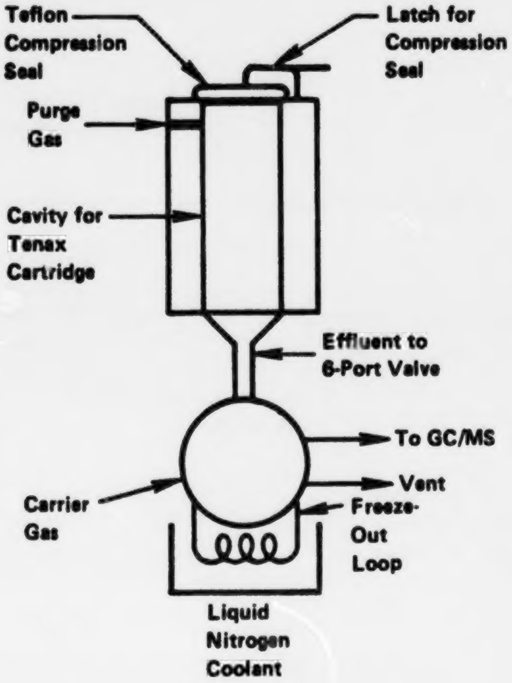

Tenax
~1.5 Grams (6 cm Bed Depth)
Glass Wool Plugs
(0.5 cm Long)
Glass Cartridge
(13.5 mm OD x
100 mm Long)

(a) Glass Cartridge

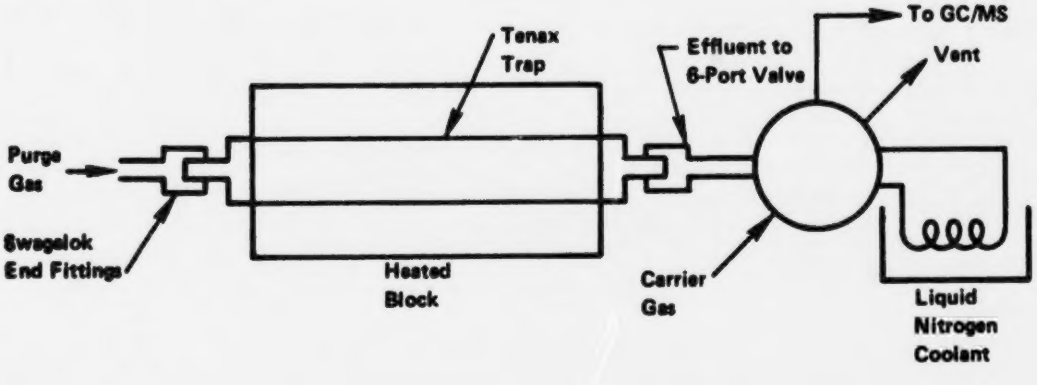

1/2" to
1/8"
Reducing
Union
Glass Wool
Plugs
(0.5 cm Long)
1/8" End Cap
1/2"
Swagelok
Fitting
Tenax
~1.5 Grams (7 cm Bed Depth)
Metal Cartridge
(12.7 mm OD x
100 mm Long)

(b) Metal Cartridge

FIGURE 1. TENAX CARTRIDGE DESIGNS

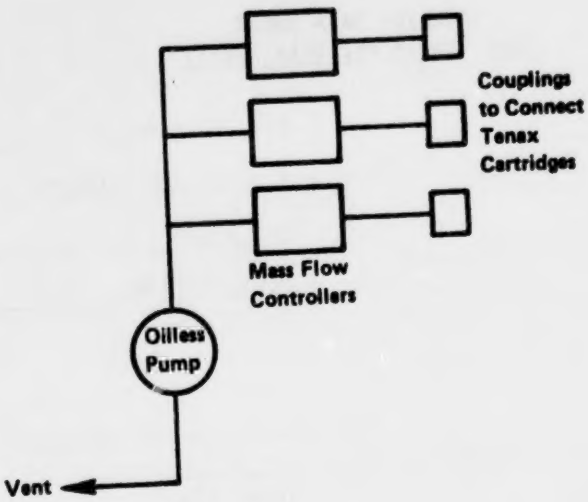

Teflon Compression Seal
Latch for Compression Seal
Purge Gas
Cavity for Tenax Cartridge
Effluent to 6-Port Valve
To GC/MS
Vent
Carrier Gas
Freeze-Out Loop
Liquid Nitrogen Coolant

(a) Glass Cartridges (Compression Fit)

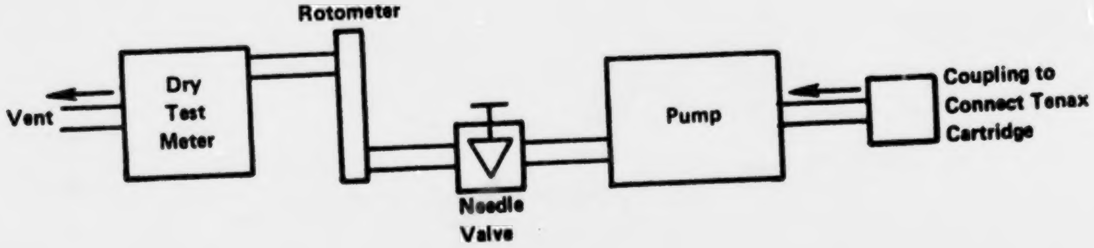

Tenax Trap
Effluent to 6-Port Valve
To GC/MS
Vent
Purge Gas
Swagelok End Fittings
Heated Block
Carrier Gas
Liquid Nitrogen Coolant

(b) Metal Cartridges (Swagelok Fittings)

FIGURE 2. TENAX CARTRIDGE DESORPTION MODULES


Couplings to Connect Tenax Cartridges
Mass Flow Controllers
Oilless Pump
Vent

(a) Mass Flow Control


Rotometer
Vent
Dry Test Meter
Needle Valve
Pump
Coupling to Connect Tenax Cartridge

(b) Needle Valve Control

FIGURE 3. TYPICAL SAMPLING SYSTEM CONFIGURATIONS

SAMPLING DATA SHEET
(One Sample Per Data Sheet)

PROJECT:______________________ DATE(S) SAMPLED:______________________

SITE:______________________ TIME PERIOD SAMPLED:______________________

LOCATION:______________________ OPERATOR:______________________

INSTRUMENT MODEL NO:______________________ CALIBRATED BY:______________________

PUMP SERIAL NO:______________________

SAMPLING DATA

Sample Number:______________________

Start Time: __________ Stop Time: __________

Time	Dry Gas Meter Reading	Rotameter Reading	Flow Rate,*Q ml/Min	Ambient Temperature °C	Barometric Pressure, mmHg	Relative Humidity, %	Comments
1.							
2.							
3.							
4.							
N.							

Total Volume Data**

V_m = (Final - Initial) Dry Gas Meter Reading, or = ______ Liters

$$= \frac{Q_1 + Q_2 + Q_3 \ldots Q_N}{N} \times \frac{1}{1000 \times (\text{Sampling Time in Minutes})} = \_\_\_\_\_\_ \text{ Liters}$$

* Flowrate from rotameter or soap bubble calibrator (specify which).

** Use data from dry gas meter if available.

FIGURE 4. EXAMPLE SAMPLING DATA SHEET

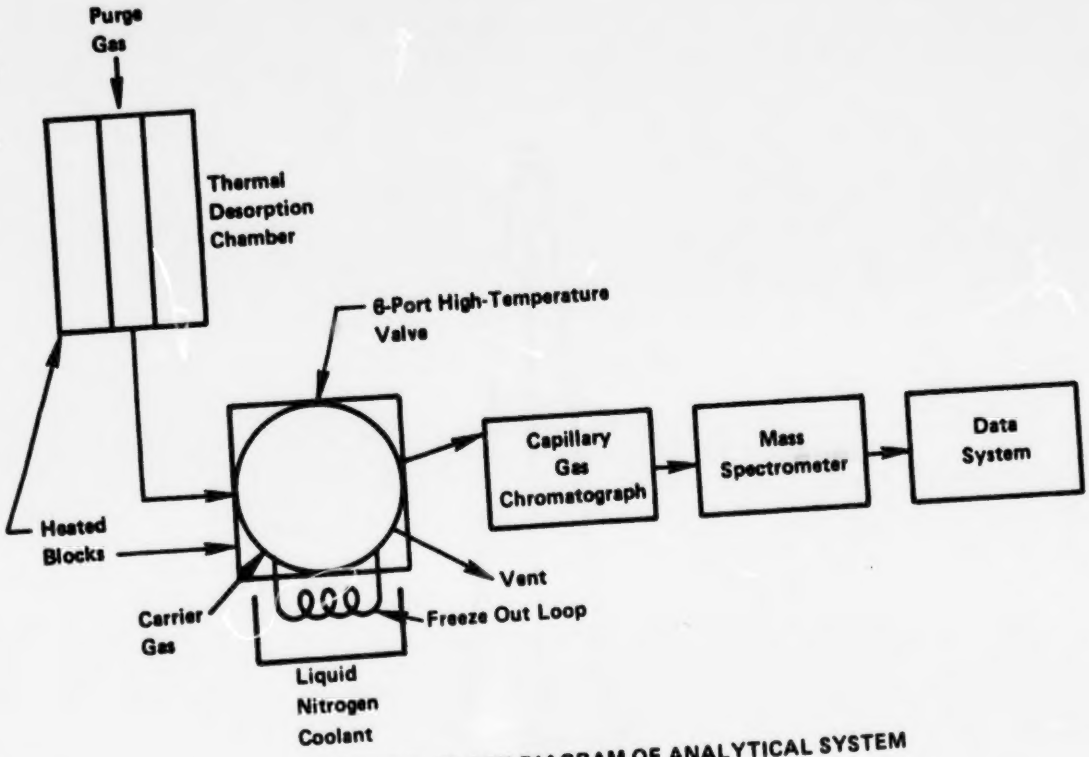
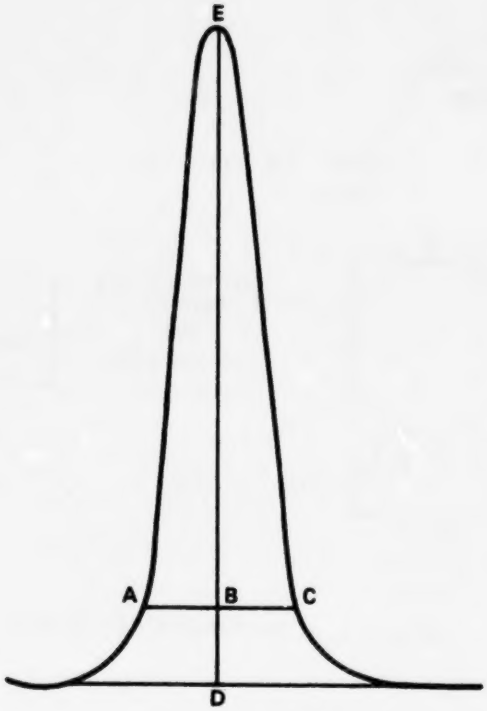

Purge Gas
Thermal Desorption Chamber
6-Port High-Temperature Valve
Capillary Gas Chromatograph
Mass Spectrometer
Data System
Heated Blocks
Vent
Freeze Out Loop
Carrier Gas
Liquid Nitrogen Coolant

FIGURE 5. BLOCK DIAGRAM OF ANALYTICAL SYSTEM



$$\text{Asymmetry Factor} = \frac{BC}{AB}$$

Example Calculation:

Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm

Therefore: $\text{Asymmetry Factor} = \frac{12}{11} = 1.1$

FIGURE 6. PEAK ASYMMETRY CALCULATION

METHOD FOR THE DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR BY CARBON MOLECULAR SIEVE ADSORPTION AND GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

1. Scope

1.1 This document describes a procedure for collection and determination of selected volatile organic compounds which can be captured on carbon molecular sieve (CMS) adsorbents and determined by thermal desorption GC/MS techniques.

1.2 Compounds which can be determined by this method are nonpolar and nonreactive organics having boiling points in the range -15 to +120°C. However, not all compounds meeting these criteria can be determined. Compounds for which the performance of the method has been documented are listed in Table 1. The method may be extended to other compounds but additional validation by the user is required. This method has been extensively used in a single laboratory. Consequently, its general applicability has not been thoroughly documented.

2. Applicable Documents

2.1 ASTM Standards

D 1356 Definitions of Terms Related to Atmospheric Sampling and Analysis.

E 355 Recommended Practice for Gas Chromatography Terms and Relationships.

2.2 Other Documents

Ambient Air Studies (1,2).

U.S. EPA Technical Assistance Document (3).

3. Summary of Method

3.1 Ambient air is drawn through a cartridge containing ~0.4 of a carbon molecular sieve (CMS) adsorbent. Volatile organic compounds are captured on the adsorbent while major inorganic atmospheric constituents pass through (or are only partially retained). After sampling, the cartridge is returned to the laboratory for analysis.

3.2 Prior to analysis the cartridge is purged with 2-3 liters of pure, dry air (in the same direction as sample flow) to remove adsorbed moisture.

3.3 For analysis the cartridge is heated to 350°-400°C, under helium purge and the desorbed organic compounds are collected in a specially designed cryogenic trap. The collected organics are then flash evaporated onto a capillary column GC/MS system (held at -70°C). The individual components are identified and quantified during a temperature programmed chromatographic run.

3.4 Due to the complexity of ambient air samples, only high resolution (capillary column) GC techniques are acceptable for most applications of the method.

4. Significance

4.1 Volatile organic compounds are emitted into the atmosphere from a variety of sources including industrial and commercial facilities, hazardous waste storage and treatment facilities, etc. Many of these compounds are toxic; hence knowledge of the concentration of such materials in the ambient atmosphere is required in order to determine human health impacts.

4.2 Traditionally air monitoring methods for volatile organic compounds have relied on carbon adsorption followed by solvent desorption and GC analysis. Unfortunately, such methods are not sufficiently sensitive for ambient air monitoring, in most cases, because only a small portion of the sample is injected onto the GC system. Recently on-line thermal desorption methods, using organic polymeric adsorbents such as Tenax® GC, have been used for ambient air monitoring. The current method uses CMS adsorbents (e.g. Spherocarb®) to capture highly volatile organics (e.g. vinyl chloride) which are not collected on Tenax®. The use of on-line thermal desorption GC/MS yields a sensitive, specific analysis procedure.

5. Definitions

Definitions used in this document and any user prepared SOPs should be consistent with ASTM D1356 (4). All abbreviations and symbols are defined with this document at the point of use.

6. Interferences

6.1 Only compounds having a mass spectrum and GC retention time similar to the compound of interest will interfere in the method. The most commonly encountered interferences are structural isomers.

6.2 Contamination of the CMS cartridge with the compound(s) of interest can be a problem in the method. The user must be careful in the preparation, storage, and handling of the cartridges through the entire process to minimize contamination.

7. Apparatus

7.1 Gas Chromatograph/Mass Spectrometry system - must be capable of subambient temperature programming. Unit mass resolution to 800 amu. Capable of scanning 30-300 amu region every 0.5-0.8 seconds. Equipped with data system for instrument control as well as data acquisition, processing and storage.

7.2 Thermal Desorption Injection Unit - Designed to accommodate CMS cartridges in use (See Figure 3) and including cryogenic trap (Figure 5) and injection valve (Carle Model 5621 or equivalent).

7.3 Sampling System - Capable of accurately and precisely drawing an air flow of 10-500 ml/minute through the CMS cartridge. (See Figure 2a or b.)

7.4 Dewar flasks - 500 mL and 5 liter.

7.5 Stopwatches.

7.6 Various pressure regulators and valves - for connecting compressed gas cylinders to GC/MS system.

7.7 Calibration gas - In aluminum cylinder. Prepared by user or vendor. For GC/MS calibration.

7.8 High pressure apparatus for preparing calibration gas cylinders (if conducted by user). Alternatively, custom prepared gas mixtures can be purchased from gas supply vendors.

7.9 Friction top can (e.g. one-gallon paint can) - With layer of activated charcoal to hold clean CMS cartridges.

7.10 Thermometer - to record ambient temperature.

7.11 Barometer (optional).

7.12 Dilution bottle - Two-liter with septum cap for standard preparation.

7.13 Teflon stirbar - 1 inch long

7.14 Gas tight syringes - 10-500 µl for standard injection onto GC/MS system and CMS cartridges.

7.15 Liquid microliter syringes - 5-50 µL for injecting neat liquid standards into dilution bottle.

7.16 Oven - 60 ± 5°C for equilibrating dilution bottle.

7.17 Magnetic stirrer.

7.18 Variable voltage transformers - (120 V and 1000 VA) and electrical connectors (or temperature controllers) to heat cartridge and cryogenic loop.

7.19 Digital pyrometer - 30 to 500°C range.

7.20 Soap bubble flow meter - 1, 10 and 100 mL calibration points.

7.21 Copper tubing (1/8 inch) and fittings for gas inlet lines.

7.22 GC column - SE-30 or alternative coating, glass capillary or fused silica.

7.23 Psychrometer (optional).

7.24 Filter holder - stainless steel or aluminum (to accommodate 1 inch diameter filter). Other sizes may be used if desired. (optional)

8. Reagents and Materials

8.1 Empty CMS cartridges - Nickel or stainless steel (See Figure 1).

8.2 CMS Adsorbent, 60/80 mesh- Spherocarb® from Analabs Inc., or equivalent.

8.3 Glasswool - silanized.

8.4 Methylene chloride - pesticide quality, or equivalent.

8.5 Gas purifier cartridge for purge and GC carrier gas containing charcoal, molecular sieves, and a drying agent. Available from various chromatography supply houses.

8.6 Helium - Ultra pure, (99.9999%) compressed gas.

8.7 Nitrogen - Ultra pure, (99.9999%) compressed gas.

8.8 Liquid nitrogen or argon (50 liter dewar).

8.9 Compressed air, if required - for operation of GC oven door.

8.10 Perfluorotributylamine (FC-43) for GC/MS calibration.

8.11 Chemical Standards - Neat compounds of interest. Highest purity available.

9. Cartridge Construction and Preparation

9.1 A suitable cartridge design in shown in Figure 1. Alternate designs have been reported (1) and are acceptable, provided the user documents their performance. The design shown in Figure 1 has a built-in heater assembly. Many users may choose to replace this heater design with a suitable separate heating block or oven to simplify the cartridge design.

9.2 The cartridge is assembled as shown in Figure 1 using standard 0.25 inch O.D. tubing (stainless steel or nickel), 1/4 inch to 1/8 inch reducing unions, 1/8 inch nuts, ferrules, and endcaps. These parts are rinsed with methylene chloride and heated at 250°C for 1 hour prior to assembly.

9.3 The thermocouple bead is fixed to the cartridge body, and insulated with a layer of Teflon tape. The heater wire (constructed from a length of thermocouple wire) is wound around the length of the cartridge and wrapped with Teflon tape to secure the wire in place. The cartridge is then wrapped with woven silica fiber insulation (Zetex or equivalent). Finally the entire assembly is wrapped with fiber glass tape.

9.4 After assembly one end of the cartridge is marked with a serial number to designate the cartridge inlet during sample collection.

9.5 The cartridges are then packed with ∿0.4 grams of CMS adsorbent. Glasswool plugs (∿0.5 inches long) are placed at each end of the cartridge to hold the adsorbent firmly in place. Care must be taken to insure that no strands of glasswool extend outside the tubing, thus causing leakage in the compression endfittings. After loading the endfittings (reducing unions and end caps) are tightened onto the cartridge.

9.6 The cartridges are conditioned for initial use by heating at 400°C overnight (at least 16 hours) with a 100 mL/minute purge of pure nitrogen. Reused cartridges need only to be heated for 4 hours and should be reanalyzed before use to ensure complete desorption of impurities.

9.7 For cartridge conditioning ultra-pure nitrogen gas is passed through a gas purifier to remove oxygen,moisture and organic contaminants. The nitrogen supply is connected to the unmarked end of the cartridge and the flow adjusted to ~50 mL/minute using a needle valve. The gas flow from the inlet (marked) end of the cartridge is vented to the atmosphere.

9.8 The cartridge thermocouple lead is connected to a pyrometer and the heater lead is connected to a variable voltage transformer (Variac) set at 0 V. The voltage on the Variac is increased to ~15 V and adjusted over a 3-4 minute period to stabilize the cartridge temperature at 380-400°C.

9.9 After 10-16 hours of heating (for new cartridges) the Variac is turned off and the cartridge is allowed to cool to ~30°C, under continuing nitrogen flow.

9.10 The exit end of the cartridge is capped and then the entire cartridge is removed from the flow line and the other endcap immediately installed. The cartridges are then placed in a metal friction top (paint) can containing ~2 inches of granulated activated charcoal (to prevent contamination of the cartridges during storage) in the bottom, beneath a retaining screen. Clean paper tissues (e.g. Kimwipes) are placed in can to avoid damage to the cartridges during shipment.

9.11 Cartridges are stored in the metal can at all times except when in use. Adhesives initially present in the cartridge insulating materials are "burnt off" during initial conditioning. Therefore, unconditioned cartridges should not be placed in the metal can since they may contaminate the other cartridges.

9.12 Cartridges are conditioned within two weeks of use. A blank from each set of cartridges is analyzed prior to use in field sampling. If an acceptable blank level is achieved, that batch of cartridges (including the cartridge serving as the blank) can be used for field sampling.

10. Sampling

10.1 Flow Rate and Total Volume Selection

10.1.1 Each compound has a characteristic retention volume (liters of air per unit weight of adsorbent). However, all of the compounds listed in Table 1 have retention volumes (at 37°C) in excess of 100 liters/cartridge (0.4 gram CMS cartridge) except vinyl chloride for which the value is ∿30 liters/cartridge. Consequently, if vinyl chloride or similarly volatile compounds are of concern the maximum allowable sampling volume is approximately 20 liters. If such highly volatile compounds are not of concern, samples as large as 100 liters can be collected.

10.1.2 To calculate the maximum allowable sampling flow rate the following equation can be used:

$$Q_{Max} = \frac{V_{Max}}{t} \times 1000$$

where

Q_{Max} is the calculated maximum sampling rate in mL/minute.
t is the desired sampling time in minutes.
V_{Max} is the maximum allowable total volume based on the discussion in 10.1.1.

10.1.3 For the cartridge design shown in Figure 1 Q_{Max} should be between 20 and 500 mL/minute. If Q_{Max} lies outside this range the sampling time or total sampling volume must be adjusted so that this criterion is achieved.

10.1.4 The flow rate calculated in 10.1.3 defines the maximum allowable flow rate. In general, the user should collect additional samples in parallel, at successive 2- to 4-fold lower flow rates. This practice serves as a quality control procedure to check on component breakthrough and related sampling and adsorption problems, and is further discussed in the literature (5).

10.2 Sample Collection

10.2.1 Collection of an accurately known volume of air is critical to the accuracy of the results. For this reason the use of mass flow controllers, rather than conventional needle valves or orifices is highly recommended, especially at low flow rates (e.g. less than 100 milliliters/minute). Figure 2a illustrates a sampling system based on mass flow controllers which readily allows for collection of parallel samples. Figure 2b shows a commercially available sampling system based on needle valve flow controllers.

10.2.2 Prior to sample collection the sampling flow rate is calibrated near the value used for sampling, with a "dummy" CMS cartridge in place. Generally calibration is accomplished using a soap bubble flow meter or calibrated wet test meter connected to the flow exit, assuming the entire flow system is sealed. ASTM Method D 3686 (4) describes an appropriate calibration scheme, not requiring a sealed flow system downstream of the pump.

10.2.3 The flow rate should be checked before and after each sample collection. Ideally, a rotameter or mass flow meter should be included in the sampling system to allow periodic observation of the flow rate without disrupting the sampling process.

10.2.4 To collect an air sample the cartridges are removed from the sealed container just prior to initiation of the collection process.

10.2.5 The exit (unmarked) end of the cartridge is connected to the sampling apparatus. The endcap is left on the sample inlet and the entire system is leak checked by activating the sampling pump and observing that no flow is obtained over a 1 minute period. The sampling pump is then shut off.

10.2.6 The endcap is removed from the cartridge, a particulate filter and holder are placed on the inlet end of the cartridge, and the sampling pump is started. In many situations a particulate filter is not necessary since the compounds of interest are in the vapor state. However, if, large amounts of particulate matter are encountered, the filter may be useful to prevent contamination of the cartridge. The following parameters are recorded on an appropriate data sheet (Figure 4): date, sampling location, time, ambient temperature, barometric pressure, relative humidity, dry gas meter reading (if applicable), flow rate, rotometer reading (if applicable), cartridge number, pump, and dry gas meter serial number.

10.2.7 The samples are collected for the desired time, periodically recording the variables listed above. At the end of the sampling period the parameters listed in 10.2.6 are recorded and the flow rate is checked. If the flows at the beginning and end of the sampling period differ by more than 10%, the cartridge should be marked as suspect.

10.2.8 The cartridges are removed (one at a time), the endcaps are replaced, and the cartridges are placed into the original container. The friction top can is sealed and packaged for immediate shipment to the analytical laboratory.

10.2.9 The average sample rate is calculated and recorded for each cartridge according to the following equation:

$$Q_A = \frac{Q_1 + Q_2 + \ldots Q_N}{N}$$

where

Q_A = Average flow rate in ml/minute.
$Q_1, Q_2, \ldots Q_N$ = Flow rates determined at beginning, end, and immediate points during sampling.

N = Number of points averaged.

10.2.10 The total volumetric flow is obtained directly from the dry gas meter or calculated and recorded for each cartridge using the following equation:

$$V_m = \frac{T \times Q_A}{1000}$$

where

V_m = Total volume sampled in liters at measured temperature and pressure.
T = Sampling time = $T_2 - T_1$, minutes.

10.2.11 The total volume sampled (V_s) at standard conditions, 760 mm Hg and 25°C, is calculated from the following equation:

$$V_s = V_m \times \frac{Pa}{760} \times \frac{298}{273 + ta}$$

where

Pa = Average barometric pressure, mm Hg
ta = Average ambient temperature, °C.

11. Sample Analysis

11.1 Sample Purging

11.1.1 Prior to analysis all samples are purged at room temperature with pure, dry air or nitrogen to remove water vapor. Purging is accomplished as described in 9.7 except that the gas flow is in the same direction as sample flow (i.e. marked end of cartridge is connected to the flow system).

11.1.2 The sample is purged at 500 mL/minute for 5 minutes. After purging the endcaps are immediately replaced. The cartridges are returned to the metal can or analyzed immediately.

11.1.3 If very humid air is being sampled the purge time may be increased to more efficiently remove water vapor. However, the sum of sample volume and purge volume must be less than 75% of the retention volume for the most volatile component of interest.

11.2 GC/MS Setup

11.2.1 Considerable variation from one laboratory to another is expected in terms of instrument configuration. Therefore, each laboratory must be responsible for verifying that their particular system yields satisfactory results. Section 14 discusses specific performance criteria which should be met.

11.2.2 A block diagram of the analytical system required for analysis of CMS cartridges is depicted in Figure 3. The thermal desorption system must be designed to accommodate the particular cartridge configuration. For the CMS cartridge design shown in Figure 1, the cartridge heating is accomplished as described in 9.8. The use of a desorption oven, in conjunction with a simplier cartridge design is also acceptable. Exposure of the sample to metal surfaces should be minimized and only stainless steel or nickel should be employed. The volume of tubing leading from the cartridge to the GC column must be minimized and all areas must be well-swept by helium carrier gas.

11.2.3 The GC column oven must be capable of being cooled to -70°C and subsequently temperature programmed to 150°C.

11.2.4 The specific GC column and temperature program employed will be dependent on the compounds of interest. Appropriate conditions are described in the literature (2). In general, a nonpolar stationary phase (e.g. SE-30, OV-1) temperature programmed from -70 to 150°C at 8°/minute will be suitable. Fused silica, bonded-phase columns are preferable to glass columns since they are more rugged and can be inserted directly into the MS ion source, thereby eliminating the need for a GC/MS transfer line. Fused silica columns are also more readily connected to the GC injection valve (Figure 3). A drawback of fused silica, bonded-phase columns is the lower capacity compared to coated, glass capillary columns. In most cases the column capacity will be less than 1 microgram injected for fused silica columns.

11.2.5 Capillary column dimensions of 0.3 mm ID and 50 meters long are generally appropriate although shorter lengths may be sufficient in many cases.

11.2.6 Prior to instrument calibration or sample analysis the GC/MS system is assembled as shown in Figure 3. Helium purge flow (through the cartridge) and carrier flow are set at approximately 50 mL/minute and 2-3 mL/minute respectively. When a cartridge is not in place a union is placed in the helium purge line to ensure a continuous inert gas flow through the injection loop.

11.2.7 Once the column and other system components are assembled and the various flows established the column temperature is increased to 250°C for approximately four hours (or overnight if desired) to condition the column.

11.2.8 The MS and data system are set up according to the manufacturer's instructions. Electron impact ionization (70eV) and an electron multiplier gain of approximately 5 x 10^4 should be employed. Once the entire GC/MS system has been setup the system is calibrated as described in Section 11.3. The user should prepare a detailed standard operating procedure (SOP) describing this process for the particular instrument being used.

11.3 GC/MS Calibration

11.3.1 Tuning and mass standardization of the MS system is performed according to manufacturer's instructions and relevant user prepared SOPs. Perfluorotributylamine (FC-43) should generally be employed as the reference compound. The material is introduced directly into the ion source through a molecular leak. The instrumental parameters (e.g., lens voltages, resolution, etc.) should be adjusted to give the relative ion abundances shown in Table 2, as well as acceptable resolution and peak shape. If these approximate relative abundances cannot be achieved, the ion source may require cleaning according to manufacturer's instructions. In the event that the user's instrument cannot achieve these relative ion abundances, but is otherwise operating properly, the user may adopt another set of relative abundances as performance criteria. However, these alternate values must be repeatable on a day-to-day basis.

11.3.2 After the mass standardization and tuning process has been completed and the appropriate values entered into the data system, the user should then calibrate the entire GC/MS system by introducing known quantities of the components of interest into the system. Three alternate procedures may be employed for the calibration process including 1) direct injection of dilute vapor phase standards, prepared in a dilution bottle or compressed gas cylinder, onto the GC column, 2) injection of dilute vapor phase standards into a flowing inert gas stream directed onto a CMS cartridge, and 3) introduction of permeation or diffusion tube standards onto a CMS cartridge. Direct injection of a compressed gas cylinder (aluminum) standard containing trace levels of the compounds of interest has been found to be the most convenient practice since such standards are stable over a several month period. The standards preparation processes for the various approaches are described in Section 13. The following paragraphs describe the instrument calibration process for these approaches.

11.3.3 If the system is to be calibrated by direct injection of a vapor phase standard, the standard, in either a compressed gas cylinder or dilution flask, is obtained as described in Section 13. The MS and data system are setup for acquisition, but the ionizer filament is shut off. The GC column oven is cooled to -70°C, the injection valve is placed in the load mode, and the cryogenic loop is immersed in liquid nitrogen or liquid argon. Liquid argon is required for standards prepared in nitrogen or air, but not for standards prepared in helium. A known volume of the standard (10-1000 mL) is injected through the cryogenic loop at a rate of 10-100 mL/minute.

11.3.4 Immediately after loading the vapor phase standard, the injection valve is placed in the inject mode, the GC program and system clock are started, and the cryogenic loop is heated to 60°C by applying voltage (15-20 volts) to the thermocouple wire heater surrounding the loop. The voltage is adjusted to maintain a loop temperature of 60°C. An automatic temperature controller can be used in place of the manual control system. After elution of unretained components (∿3 minutes after injection) the ionizer filament is turned on and data acquisition is initiated. The helium purge line (set at 50 mL/minute) is connected to the injection valve and the valve is returned to the load mode. The loop temperature is increased to 150 °C, with helium purge, and held at this temperature until the next sample is to be loaded.

11.3.5 After the last component of interest has eluted, acquisition is terminated and the data is processed as described in Section 11.3.8. The standard injection process is repeated using different standard concentrations and/or volumes to cover the analytical range of interest.

11.3.6 If the system is to be calibrated by analysis of standard CMS cartridges, a series of cartridges is prepared as described in Sections 13.2 or 13.3. Prior to analysis the cartridges are stored (no longer than 48 hours) as described in Section 9.10. For analysis the injection valve is placed in the load mode and the cryogenic loop is immersed in liquid nitrogen (or liquid argon if desired). The CMS cartridge is installed in the helium purge line (set at 50 mL/minute) so that the helium flow through the cartridge is opposite to the direction of sample flow and the purge gas is directed through the cryogenic loop and vented to the atmosphere. The CMS cartridge is heated to 370-400°C and maintained at this temperature for 10 minutes (using the temperature control process described in Section 9.8). During the desorption period, the GC column oven is cooled to -70°C and the MS and data system are setup for acquisition, but the ionizer filament is turned off.

11.3.7 At the end of the 10 minute desorption period, the analytical process described in Sections 11.3.4 and 11.3.5 is conducted. During the GC/MS analysis heating of the CMS cartridge is discontinued. Helium flow is maintained through the CMS cartridge and cryogenic loop until the cartridge has cooled to room temperature. At that time, the cryogenic loop is allowed to cool to room temperature and the system is ready for further cartridge analysis. Helium flow is maintained through the cryogenic loop at all times, except during the installation or removal of a CMS cartridge, to minimize contamination of the loop.

11.3.8 Data processing for instrument calibration involves determining retention times, and integrated characteristic ion intensities for each of the compounds of interest. In addition, for at least one chromatographic run, the individual mass spectra should be inspected and compared to reference spectra to ensure proper instrumental performance. Since the steps involved in data processing are highly instrument specific, the user should prepare a SOP describing the process for individual use. Overall performance criteria for instrument calibration are provided in Section 14. If these criteria are not achieved, the user should refine the instrumental parameters and/or operating procedures to meet these criteria.

11.4 Sample Analysis

11.4.1 The sample analysis is identical to that described in Sections 11.3.6 and 11.3.7 for the analysis of standard CMS cartridges.

11.4.2 Data processing for sample data generally involves 1) qualitatively determining the presence or absence of each component of interest on the basis of a set of characteristic ions and the retention time using a reversed-search software routine, 2) quantification of each identified component by integrating the intensity of a characteristic ion and comparing the value to that of the calibration standard, and 3) tentative identification of other components observed using a forward (library) search software routine. As for other user specific processes, a SOP should be prepared describing the specific operations for each individual laboratory.

12. Calculations

12.1 Calibration Response Factors

12.1.1 Data from calibration standards is used to calculate a response factor for each component of interest. Ideally the process involves analysis of at least three calibration levels of each component during a given day and determination of the response factor (area/nanogram injected) from the linear least squares fit of a plot of nanograms injected versus area (for the characteristic ion). In general, quantities of components greater than 1,000 nanograms should not be injected because of column overloading and/or MS response nonlinearity.

12.1.2 In practice the daily routine may not always allow analysis of three such calibration standards. In this situation calibration data from consecutive days may be pooled to yield a response factor, provided that analysis of replicate standards of the same concentration are shown to agree within 20% on the consecutive days. In all cases one given standard concentration, near the midpoint of the analytical range of interest, should be injected at least once each day to determine day-to-day precision of response factors.

12.1.3 Since substantial nonlinearity may be present in the calibration curve, a nonlinear least squares fit (e.g. quadratic) should be employed. This process involves fitting the data to the following equation:

$$Y = A + BX + CX^2$$

where

Y = peak area
X = quantity of component injected nanograms
A, B, and C are coefficients in the equation.

12.2 Analyte Concentrations

12.2.1 Analyte quantities on a sample cartridge are calculated from the following equation:

$$Y_A = A + BX_A + CX^2$$

where Y_A is the area of the analyte characteristic ion for the sample cartridge.
X_A is the calculated quantity of analyte on the sample cartridge, in nanograms.
A, B, and C are the coefficients calculated from the calibration curve described in Section 12.1.3.

12.2.2 If instrumental response is essentially linear over the concentration range of interest, a linear equation (C=0 in the equation above) can be employed.

12.2.3 Concentration of analyte in the original air sample is calculated from the following equation:

$$C_A = \frac{X_A}{V_s}$$

where

C_A is the calculated concentration of analyte in ng/L.

Vs and X_A are as previously defined in Section 10.2.11 and 12.2.1, respectively.

13. Standard Preparation

13.1 Standards for Direct Injection

13.1.1 Standards for direct injection can be prepared in compressed gas cylinders or in dilution vessels. The dilution flask protocol has been described in detail in another method and is not repeated here (6). For the CMS method where only volatile compounds (boiling point <120°C) are of concern, the preparation of dilute standards in 15 liter aluminum compressed gas cylinders has been found to be most convenient. These standards are generally stable over at least a 3-4 month period and in some cases can be purchased from commercial suppliers on a custom prepared basis.

13.1.2 Preparation of compressed gas cylinders requires working with high pressure tubing and fittings, thus requiring a user prepared SOP which ensures that adequate safety precautions are taken. Basically, the preparation process involves injecting a predetermined amount of neat liquid or gas into an empty high pressure cylinder of known volume, using gas flow into the cylinder to complete the transfer.

The cylinder is then pressurized to a given value (500-1000 psi). The final cylinder pressure must be determined using a high precision gauge after the cylinder has thermally equilibrated for a 1-2 hour period after filling.

13.1.2 The concentration of components in the cylinder standard should be determined by comparison with National Bureau of Standards reference standards (e.g. SRM 1805-benzene in nitrogen) when available.

13.1.3 The theoretical concentration (at 25°C and 760 mm pressure) for preparation of cylinder standards can be calculated using the following equation:

$$C_T = \frac{V_I \times d}{V_c} \times \frac{14.7}{P_c + 14.7} \times 24.4 \times 1000$$

where C_T is the component concentration, in ng/mL at 25°C and 760 mm Hg pressure.

V_I is the volume of neat liquid component injected, in µL.

V_c is the internal volume of the cylinder, in L.

d is the density of the neat liquid component, in g/mL.

P_c is the final pressure of the cylinder standards, in pounds per square inch gauge (psig).

13.2 Preparation of Spiked Traps by Vapor Phase Injection

This process involves preparation of a dilution flask or compressed gas cylinder containing the desired concentrations of the compound(s) of interest and injecting the desired volume of vapor into a flowing gas stream which is directed onto a clean CMS cartridge. The procedure is described in detail in another method within the Compendium (6) and will not be repeated here.

13.3 Preparation of Spiked Traps Using Permeation or Diffusion Tubes

13.3.1 A flowing stream of inert gas containing known amounts of each compound of interest is generated according to ASTM Method D3609 (4). Note that a method of accurately maintaining temperature within ± 0.1°C is required and the system generally must be equilibrated for at least 48 hours before use.

13.3.2 An accurately known volume of the standard gas stream (usually 0.1-1 liter) is drawn through a clean CMS cartridge using the sampling system described in Section 10.2.1, or a similar system. However, if mass flow controllers are employed, they must be calibrated for the carrier gas used in Section 13.3.1 (usually nitrogen). Use of air as the carrier gas for permeation systems is not recommended, unless the compounds of interest are known to be highly stable in air.

13.3.3 The spiked traps are then stored or immediately analyzed as in Sections 11.3.6 and 11.3.7.

14. Performance Criteria and Quality Assurance

This section summarizes the quality assurance (QA) measures and provides guidance concerning performance criteria which should be achieved within each laboratory. In many cases the specific QA procedures have been described within the appropriate section describing the particular activity (e.g. parallel sampling).

14.1 Standard Operating Procedures (SOPs)

14.1.1 Each user should generate SOPs describing the following activities as accomplished in their laboratory: 1) assembly, calibration and operation of the sampling system, 2) preparation, handling and storage of CMS cartridges, 3) assembly and operation of GC/MS system including the thermal desorption apparatus and data system, and 4) all aspects of data recording and processing.

14.1.2 SOPs should provide specific stepwise instructions and should be readily available to, and understood by the laboratory personnel conducting the work.

14.2 CMS Cartridge Preparation

14.2.1 Each batch of CMS cartridges, prepared as described in Section 9, should be checked for contamination by analyzing one cartridge, immediately after preparation. While analysis can be accomplished by GC/MS, many laboratories may chose to use GC/FID due to logistical and cost considerations.

14.2.2 Analysis by GC/FID is accomplished as described for GC/MS (Section 11) except for use of FID detection.

14.2.3 While acceptance criteria can vary depending on the components of interest, at a minimum the clean cartridge should be demonstrated to contain less than one-fourth of the minimum level of interest for each component. For most compounds the blank level should be less than 10 nanograms per cartridge in order to be acceptable. More rigid criteria may be adopted, if necessary, within a specific laboratory. If a cartridge does not meet these acceptance criteria, the entire lot should be rejected.

14.3 Sample Collection

14.3.1 During each sampling event at least one clean cartridge will accompany the samples to the field and back to the laboratory, having been placed in the sampler but without sampling air, to serve as a field blank. The average amount of material found on the field blank cartridges may be subtracted from the amount found on the actual samples. However, if the blank level is greater than

25% of the sample amount, data for that component must be identified as suspect.

14.3.2 During each sampling event at least one set of parallel samples (two or more samples collected simultaneously) should be collected, preferably at different flow rates as described in Section 10.1.4. If agreement between parallel samples is not generally within ±25% the user should collect parallel samples on a much more frequent basis (perhaps for all sampling points). If a trend of lower apparent concentrations with increasing flow rate is observed for a set of parallel samples one should consider using a reduced sampling rate and longer sampling interval, if possible. If this practice does not improve the reproducibility further evaluation of the method performance for the compound of interest might be required.

14.3.3 Backup cartridges (two cartridges in series) should be collected with each sampling event. Backup cartridges should contain less than 10% of the amount of components of interest found in the front cartridges, or be equivalent to the blank cartridge level, whichever is greater.

14.4 GC/MS Analysis

14.4.1 Performance criteria for MS tuning and mass standardization have been discussed in Section 11.2 and Table 2. Additional criteria can be used by the laboratory, if desired. The following sections provide performance guidance and suggested criteria for determining the acceptability of the GC/MS system.

14.4.2 Chromatographic efficiency should be evaluated daily by the injection of calibration standards. A reference compound(s) should be chosen from the calibration standard and plotted on an expanded time scale so that its width at 10% of the peak height can be calculated, as shown in Figure 6. The width of the peak at 10% height should not exceed 10 seconds. More stringent criteria may be required for certain applications. The asymmetry factor (see Figure 6) should be between 0.8 and 2.0. The user should also evaluate chromatographic performance for any polar or reactive compounds of interest, using the process described above. If peaks are observed that exceed the peak width or asymmetry factor criteria above, one should inspect the entire system to determine if unswept zones or cold spots are present in any of the fittings or tubing and/or if replacement of the GC column is required. Some laboratories may chose to evaluate column performance separately by direct injection of a test mixture onto the GC column. Suitable schemes for column evaluation have been reported in the literature (7).

14.4.3 The detection limit for each component is calculated from the data obtained for calibration standards. The detection limit is defined as

$$DL = A + 3.3S$$

where

DL is the calculated detection limit in nanograms injected.

A is the intercept calculated in Section 12.1.3.

S is the standard deviation of replicate determinations of the lowest level standard (at least three such determinations are required). The lowest level standard should yield a signal to noise ratio (from the total ion current response) of approximately 5.

14.4.4 The relative standard deviation for replicate analyses of cartridges spiked at approximately 10 times the detection limit should be 20% or less. Day to day relative standard deviation for replicate cartridges should be 25% or less.

14.4.5 A useful performance evaluation step is the use of an internal standard to track system performance. This is accomplished by spiking each cartridge, including blank, sample, and calibration cartridges with approximately 100 nanograms of a compound not generally present is ambient air (e.g. perfluorotoluene). Spiking is readily accomplished using the procedure outlined in Section 13.2, using a compressed gas standard. The integrated ion intensity for this compound helps to identify problems with a specific sample. In general the user should calculate the standard deviation of the internal standard response for a given set of samples analyzed under identical tuning and calibration conditions. Any sample giving a value greater than ± 2 standard deviations from the mean (calculated excluding that particular sample) should be identified as suspect. Any marked change in internal standard response may indicate a need for instrument recalibration.

14.5 Method Precision and Recovery

14.5.1 Recovery and precision data for selected volatile organic compounds are presented in Table 1. These data were obtained using ambient air, spiked with known amounts of the compounds in a dynamic mixing system (2).

14.5.2 The data in Table 1 indicate that in general recoveries better than 75% and precision (relative standard deviations) of 15-20% can be obtained. However, selected compounds (e.g. carbon tetrachloride and benzene) will have poorer precision and/or recovery. The user must check recovery and precision for any compounds for which quantitative data are needed.

References

1. Kebbekus, B. B. and J. W. Bozzelli. Collection and Analysis of Selected Volatile Organic Compounds in Ambient Air. Proceedings of Air Pollution Control Association, Paper No. 82-65.2, Air Pollution Control Association, Pittsburgh, Pennsylvania, 1982.

2. Riggin R. M. and L. E. Slivon. Determination of Volatile Organic Compounds in Ambient Air Using Carbon Molecular Sieve Adsorbants, Special Report on Contract 68-02-3745 (WA-7), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, September, 1983.

3. Riggin, R. M., "Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air", EPA-600/4-83-027, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1983.

4. Annual Book of ASTM Standards, Part 11.03, "Atmospheric Analysis: Occupational Health and Safety", American Society for Testing and Materials, 1983.

5. Walling, J. F., Berkley, R. E., Swanson, D. H., and Toth, F. J. "Sampling Air for Gaseous Organic Chemical-Applications to Tenax", EPA-600/7-54-82-059, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1982.

6. This Methods Compendium - Tenax Method (TO 1).

7. Grob, K., Jr., Grob, G., and Grob, K., "Comprehensive Standardized Quality Test for Glass Capillary Columns", J. Chromatog., 156 1-20, 1978.

TABLE 1. VOLATILE ORGANIC COMPOUNDS FOR WHICH THE CMS ADSORPTION METHOD HAS BEEN EVALUATED

Compound	Retention Time, Minutes(a)	Characteristic Mass Fragment Used For Quantification	Method Performance Data(b)		
			Concentration, ng/L	Percent Recovery	Standard Deviation
Vinyl Chloride	6.3	62	17	74	19
Acrylonitrile	10.8	53	20	85	18
Vinylidene Chloride	10.9	96	36	94	19
Methylene Chloride	11.3	84	28	93	16
Allyl Chloride	11.4	76	32	72	19
Chloroform	13.8	83	89	91	12
1,2-Dichloroethane	14.5	62	37	85	11
1,1,1-Trichloroethane	14.7	97	100	75	9.1
Benzene	15.4	78	15	140	37
Carbon Tetrachloride	15.5	117	86	55	2.9
Toluene	18.0	91	4.1	98	5.4

a) GC conditions as follows:

Column - Hewlett Packard, crosslinked methyl silicone, 0.32 mm ID x 50 mm long, thick film, fused silica.

Temperature Program - 70°C for 2 minutes then increased at 8°C/minute to 120°C.

b) From Reference 2. For spiked ambient air.

TABLE 2. SUGGESTED PERFORMANCE CRITERIA FOR RELATIVE ION ABUNDANCES FROM FC-43 MASS CALIBRATION

M/E	% Relative Abundance
51	1.8 ± 0.5
69	100
100	12.0 ± 1.5
119	12.0 ± 1.5
131	35.0 ± 3.5
169	3.0 ± 0.4
219	24.0 ± 2.5
264	3.7 ± 0.4
314	0.25 ± 0.1

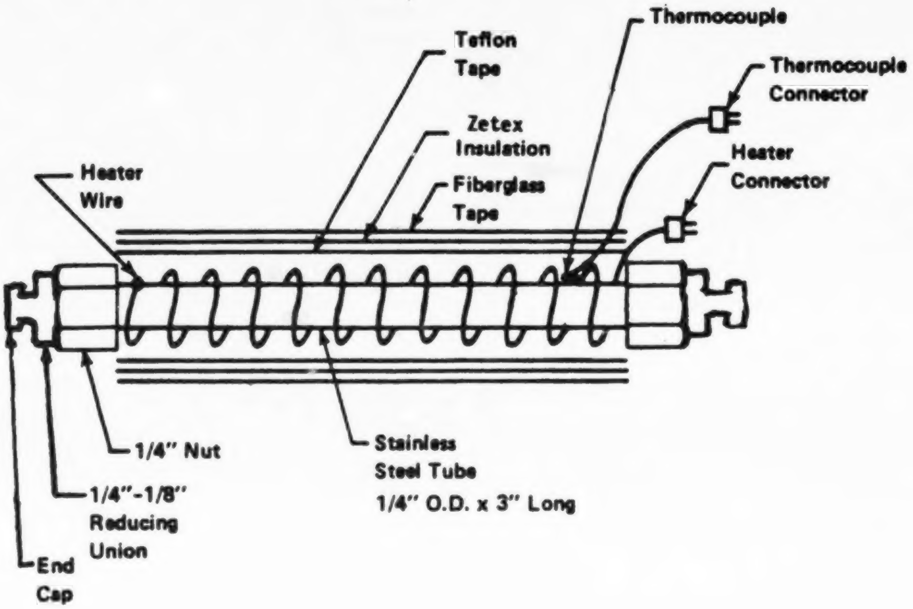
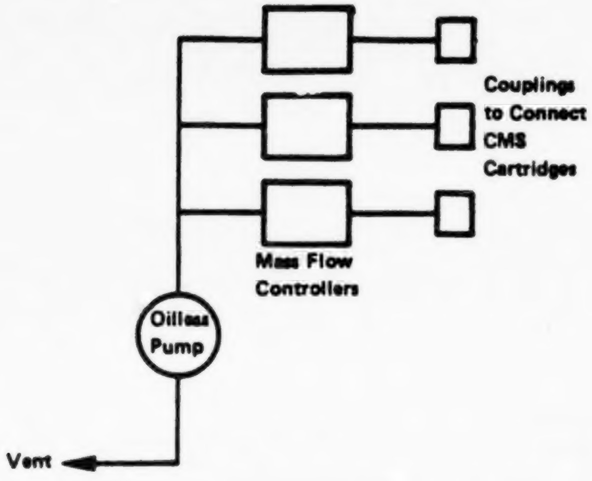
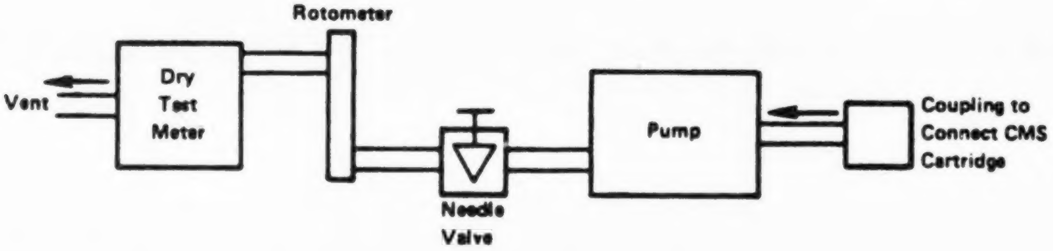

Thermocouple
Teflon Tape
Thermocouple Connector
Zetex Insulation
Heater Connector
Heater Wire
Fiberglass Tape
1/4" Nut
Stainless Steel Tube 1/4" O.D. x 3" Long
1/4"-1/8" Reducing Union
End Cap

FIGURE 1. DIAGRAM SHOWING CARBON MOLECULAR SIEVE TRAP (CMS) CONSTRUCTION


Couplings
to Connect
CMS
Cartridges
Mass Flow
Controllers
Oilless
Pump
Vent

(a) Mass Flow Control


Rotometer
Vent
Dry
Test
Meter
Needle
Valve
Pump
Coupling to
Connect CMS
Cartridge

(b) Needle Valve Control

FIGURE 2. TYPICAL SAMPLING SYSTEM CONFIGURATIONS

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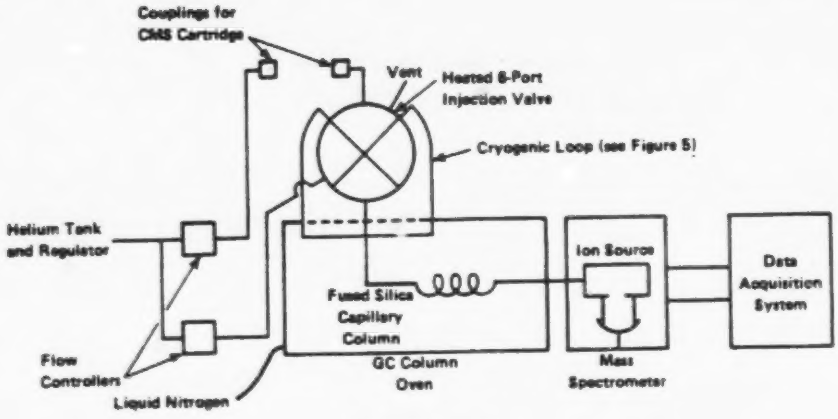
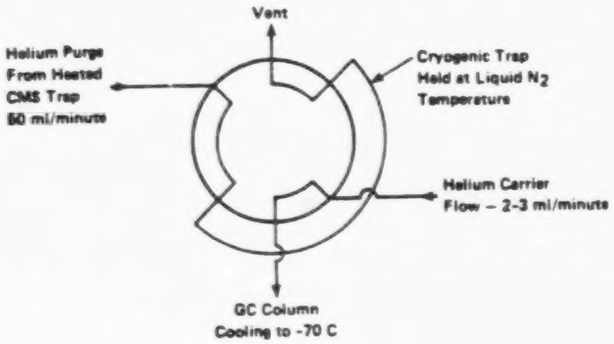
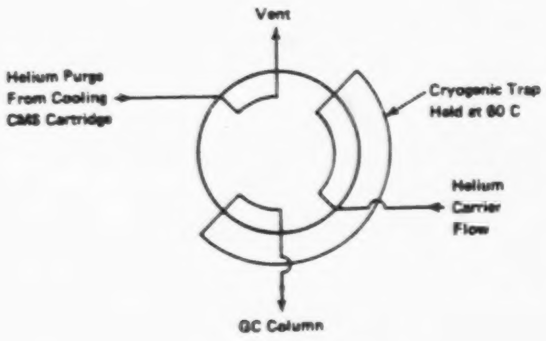
best available copy.


Couplings for
CMS Cartridge
Vent
Heated 6-Port
Injection Valve
Cryogenic Loop (see Figure 5)
Helium Tank
and Regulator
Ion Source
Data
Acquisition
System
Fused Silica
Capillary
Column
Flow
Controllers
GC Column
Oven
Mass
Spectrometer
Liquid Nitrogen

(a) Overall System


Vent
Helium Purge
From Heated
CMS Trap
60 ml/minute
Cryogenic Trap
Held at Liquid N_2
Temperature
Helium Carrier
Flow – 2-3 ml/minute
GC Column
Cooling to -70 C

(b) Valve – Load Mode


Vent
Helium Purge
From Cooling
CMS Cartridge
Cryogenic Trap
Held at 60 C
Helium
Carrier
Flow
GC Column

(c) Valve – Inject Mode

FIGURE 3. GC/MS ANALYSIS SYSTEM FOR CMS CARTRIDGES

SAMPLING DATA SHEET
(One Sample Per Data Sheet)

PROJECT:____________________ DATE(S) SAMPLED:____________________

SITE:____________________ TIME PERIOD SAMPLED:____________________

LOCATION:____________________ OPERATOR:____________________

INSTRUMENT MODEL NO:____________________ CALIBRATED BY:____________________

PUMP SERIAL NO:____________________

SAMPLING DATA

Sample Number:____________________

Start Time: __________ Stop Time: __________

Time	Dry Gas Meter Reading	Rotameter Reading	Flow Rate,*Q ml/Min	Ambient Temperature °C	Barometric Pressure, mmHg	Relative Humidity, %	Comments
1.							
2.							
3.							
4.							
N.							

Total Volume Data**

V_m = (Final - Initial) Dry Gas Meter Reading, or = ______ Liters

$$\frac{Q_1 + Q_2 + Q_3 \ldots Q_N}{N} \times \frac{1}{1000 \times (\text{Sampling Time in Minutes})} = \_\_\_\_\_\_ \text{ Liters}$$

* Flowrate from rotameter or soap bubble calibrator (specify which).

** Use data from dry gas meter if available.

FIGURE 4. EXAMPLE SAMPLING DATA SHEET

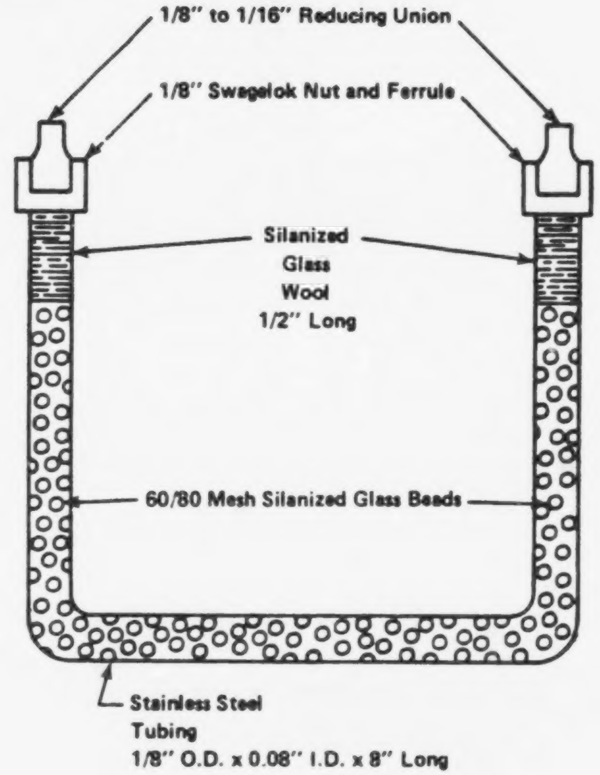
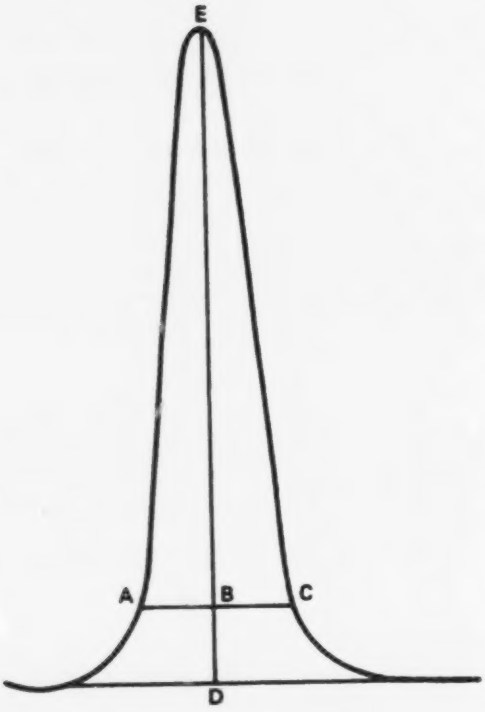

1/8" to 1/16" Reducing Union
1/8" Swagelok Nut and Ferrule
Silanized Glass Wool 1/2" Long
60/80 Mesh Silanized Glass Beads
Stainless Steel Tubing 1/8" O.D. x 0.08" I.D. x 8" Long

FIGURE 5. CRYOGENIC TRAP DESIGN



Asymmetry Factor = $\frac{BC}{AB}$

Example Calculation:

Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm

Therefore: Asymmetry Factor = $\frac{12}{11}$ = 1.1

FIGURE 6. PEAK ASYMMETRY CALCULATION

METHOD FOR THE DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR USING CRYOGENIC PRECONCENTRATION TECHNIQUES AND GAS CHROMATOGRAPHY WITH FLAME IONIZATION AND AND ELECTRON CAPTURE DETECTION

1. Scope

1.1 This document describes a method for the determination of highly volatile compounds having boiling points in the range of -10 to 200°C.

1.2 The methodology detailed in this document is currently employed by numerous laboratories (1-4;8-11). Modifications to this methodology should be accompanied by appropriate documentation of the validity and reliability of these changes.

2. Applicable Documents

2.1 ASTM Standards

D1356 Definition of Terms Related to Atmospheric Sampling and Analysis

E 355 Recommended Practice for Gas Chromatography Terms and Relationships

2.2 Other Documents

Ambient Air Studies (1-4).

U. S. EPA Technical Assistance Document (5).

3. Summary of Method

3.1 Ambient air analyses are performed as follows. A collection trap, as illustrated in Figure 1, is submerged in either liquid oxygen or argon. Liquid argon is highly recommended for use because of the safety hazard associated with liquid oxygen. With the sampling valve in the fill position an air sample is then admitted into the trap by a volume measuring apparatus. In the meantime, the column oven is cooled to a sub-ambient temperature (-50°C). Once sample collection is completed, the valve is switched so that the carrier gas sweeps the contents of the trap onto the head of the cooled GC column. Simultaneously, the liquid cryogen is removed and the trap is heated to assist the sample transfer process. The GC column is temperature programmed and the component peaks eluting from the columns are identified and quantified using flame ionization and/or electron capture detection. Alternate detectors (e.g. photoionization) can be used as appropriate. An automated system incorporating these various operations as well as the data processing function has been described in the literature (8,9).

3.2 Due to the complexity of ambient air samples, high resolution (capillary column) GC techniques are recommended. However, when highly selective detectors (such as the electron capture detector) are employed, packed column technology without cryogenic temperature programming can be effectively utilized in some cases.

4. Significance

4.1 Volatile organic compounds are emitted into the atmosphere from a variety of sources including industrial and commercial facilities, hazardous waste storage facilities, etc. Many of these compounds are toxic, hence knowledge of the levels of such materials in the ambient atmosphere is required in order to determine human health impacts.

4.2 Because these organic species are present at ppb levels or below, some means of sample preconcentration is necessary in order to acquire sufficient material for identification and quantitation. The two primary preconcentration techniques are cryogenic collection and the use of solid adsorbents. The method described herein involves the former technique.

5. Definitions

Definitions used in this document and any user prepared SOPs should be consistent with ASTM D1356 (6). All abbreviations and symbols are defined within this document at the point of use.

6. Interferences/Limitations

6.1 Compounds having similar GC retention times will interfere in the method. Replacing the flame ionization detector with more selective detection systems will help to minimize these interferences. Chlorinated species, in particular, should be determined using the electron capture detector to avoid interference from volatile hydrocarbons.

6.2 An important limitation of the technique is the condensation of moisture in the collection trap. The possibility of ice plugging the trap and stopping the flow is of concern, and water subsequently transferred to the capillary column may also result in flow stoppage and cause deleterious effects to certain column materials. Use of permaselective Nafion® tubing in-line before the cryogenic trap avoids this problem; however, the material must be used with caution because of possible loses of certain compounds. Another potential problem is contamination from the Nafion ® tubing. The user should consult the literature (7-12) for details on the use of permeation-type driers.

7. Apparatus

7.1 Gas chromatograph/Flame Ionization/Electron Capture Detection System- must be capable of subambient temperature programming. A recent publication (8) describes an automated GC system in which the cyrogenic sampling and analysis features are combined. This system allows simultaneous flame ionization and electron capture detection.

7.2 Six-port sampling valve - modified to accept a sample collection trap (Figure 1).

7.3 Collection trap - 20 cm x 0.2 cm I.D. stainless steel tubing packed with 60/80 mesh silanized glass beads and sealed with glass wool. For the manual system (Section 9.2) the trap is externally wrapped with 28 gauge (duplex and fiberglass insulated) type "K" thermocouple wire. This wire, beaded at one end, is connected to a powerstat during the heating cycle. A thermocouple is also attached to the trap as shown in Figure 1.

7.4 Powerstat - for heating trap.

7.5 Temperature readout device - for measuring trap temperature during heating cycle.

7.6 Glass dewar flask - for holding cryogen.

7.7 Sample volume measuring apparatus - capable of accurately and precisely measuring a total sample volume up to 500 cc at sampling rates between 10 and 200 cc/minute. See Section 9.

7.8 Stopwatch.

7.9 Dilution container for standards preparation - glass flasks or Teflon (Tedlar) bags, .002 inch film thickness (see Figure 2).

7.10 Liquid microliter syringes - 5-50 µl for injecting liquid standards into dilution container.

7.11 Volumetric flasks - various sizes, 1-10 mL.

7.12 GC column - Hewlett Packard 50 meter methyl silicone cross-linked fused silica column (.3 mm I.D., thick film) or equivalent.

7.13 Mass flow controller - 10-200 mL/minute flow control range.

7.14 Permeation drier - PermaPure® - Model MD-125F, or equivalent. Alternate designs described in the literature (7-12) may also be acceptable.

8. Reagents and Materials

8.1 Glass beads - 60/80 mesh, silanized.

8.2 Glasswool - silanized.

8.3 Helium - zero grade compressed gas, 99.9999%.

8.4 Hydrogen - zero grade compressed gas, 99.9999%.

8.5 Air - zero grade compressed gas.

8.6 Liquid argon (or liquid oxygen).

8.7 Liquid nitrogen.

8.8 SRM 1805 - benzene in nitrogen standard. Available from the National Bureau of Standards. Additional such standards will become available in the future.

8.9 Chemical standards - neat compounds of interest, highest purity available.

9. Sampling and Analysis Apparatus

Two systems are described below which allow collection of an accurately known volume of air (100-1000 mL) onto a cryogenically cooled trap. The first system (Section 9.1) is an automated device described in the literature (8,9). The second system (Section 9.2) is a manual device, also described in the literature (2).

9.1 The automated sampling and analysis system is shown in Figure 3. This system is composed of an automated GC system (Hewlett Packard Model 5880A, Level 4, or equivalent) and a sample collection system (Nutech Model 320-01, or equivalent). The overall system is described in the literature (8).

9.1.1 The electronic console of the sampling unit controls the mechanical operation of the six-port valve and cryogenic trapping components as well as the temperatures in each of the three zones (sample trap, transfer line, and valve).

9.1.2 The valve (six-port air activated, Seiscor Model 8 or equivalent) and transfer line are constantly maintained at 120°C. During sample collection the trap temperature is maintained at -160 ± 5°C by a flow of liquid nitrogen controlled by a solenoid valve. A cylindrical 250 with heater, held in direct contact with the trap, is used to heat the trap to 120°C in 60 seconds or less during the sample desorption step. The construction of the sample trap is described in Section 7.3.

9.1.3 The sample flow is controlled by a pump/mass flow controller assembly, as shown in Figure 3. A sample flow of 10-100 mL/minute is generally employed, depending on the desired sampling period. A total volume of 100-1000 mL is commonly collected.

9.1.4 In many situations a permaselective drier (e.g. Nafion®) may be required to remove moisture from the sample. Such a device is installed at the sample inlet. Two configurations for such devices are available. The first configuration is the tube and shell type in which the sample flow tube is surrounded by an outer shell through which a countercurrent flow of clean, dry air is maintained. The dry air stream must be free from contaminants and its flow rate should be 3-4 times greater than the sample flow to achieve effective drying. A second configuration (7) involves placing a drying agent, e.g. magnesium carbonate, on the outside of the sample flow tube. This approach eliminates the need for a source of clean air in the field. However, contamination from the drying agent can be a problem.

9.2 The manual sampling consists of the sample volume measuring apparatus shown in Figure 4 connected to the cryogenic trap/ GC assembly shown in Figure 1. The operation of this assembly is described below.

9.2.1 Pump-Down Position

The purpose of the pump-down mode of operation is to evacuate the ballast tank in preparation for collecting a sample as illustrated in Figure 4. (While in this position, helium can also be utilized to backflush the sample line, trap, etc. However, this cleaning procedure is not normally needed during most sampling operations). The pump used for evacuating the system should be capable of attaining 200 torr pressure.

9.2.2 Volume Measuring Position

Once the system has been sufficiently evacuated, the 4-way ball valve is switched to prepare for sample collection. The 3-position valve is used to initiate sample flow while the needle valve controls the rate of flow.

9.2.3 Sample Volume Calculation

The volume of air that has passed through the collection trap corresponds to a known change in pressure within the ballast tank (as measured by the Wallace Tiernan gauge). Knowing the volume, pressure change, and temperature of the system, the ideal gas law can be used to calculate the number of moles of air sampled. On a volume basis, this converts to the following equation:

$$V_s = \frac{\Delta P}{760} \times \frac{298}{T_A + 273}$$

where

V_s = Volume sampled at 760 mm Hg pressure and 25°C.

ΔP = Change in pressure within the ballast tank, mm of Hg.

V = Volume of ballast tank and gauge.

T_A = Temperature of ballast tank, °C.

The internal volume of the ballast tank and gauge can be determined either by H_2O displacement or by injecting calibrated volumes of air into the system using large volume syringes, etc.

10. Sampling and Analysis Procedure - Manual Device

10.1 This procedure assumes the use of the manual sampling system described in Section 9.2

10.2 Prior to sample collection, the entire assembly should be leak-checked. This task is accomplished by sealing the sampling inlet line, pumping the unit down and placing the unit in the flow measuring mode of operation. An initial reading on the absolute pressure gauge is taken and rechecked after 10 minutes. No apparent change should be detected.

10.3 Preparation for sample collection is carried out by switching the 6-port valve to the "fill" position and connecting the heated sample line to the sample source. Meanwhile the collection trap is heated to 150°C (or other appropriate temperature). The volume measuring apparatus is pumped-down and switched to the flow measuring mode. The 3-position valve is opened and a known volume of sample is then passed through the heated sample line and trap to purge the system.

10.4 After the system purge is completed, the 3-position valve is closed and the corresponding gauge pressure is recorded. The collection trap is then immersed into a dewar of liquid argon (or liquid oxygen) and the 3-position valve is temporarily opened to draw in a known volume of air, i.e. a change in pressure corresponds to a specific volume of air (see Section 9). Liquid nitrogen cannot be used as the cryogen since it will also condense oxygen from the air. Liquid oxygen represents a potential fire hazard and should not be employed unless absolutely necessary.

10.5 After sample collection is completed, the 6-port valve is switched to the inject position, the dewar is removed and the trap is heated to 150°C to transfer the sample components to the head of the GC column which is initially maintained at -50°C. Temperature programming is initiated to elute the compounds of interest.

10.6 A GC integrator (or data system if available) is activated during the injection cycle to provide component identification and quantitation.

11. Sampling and Analysis Procedure - Automated Device

11.1 This procedure assumes the use of the automated system shown in Figure 3. The components of this system are discussed in Section 9.1.

11.2 Prior to initial sample collection the entire assembly should be leak-checked. This task is completed by sealing the sample inlet line and noting that the flow indication or the mass flow controller drops to zero (less than 1 mL/minute).

11.3 The sample trap, valve, and transfer line are heated to 120°C and ambient air is drawn through the apparatus (∿60 mL/minute) for a period of time 5-10 minutes to flush the system, with the sample valve in the inject position. During this time the GC column is maintained at 150°C to condition the column.

11.4 The sample trap is then cooled to -160 ± 5°C using a controlled flow of liquid nitrogen. Once the trap temperature has stabilized, sample flow through the trap is initiated by placing the valve in the inject position and the desired volume of air is collected.

11.5 During the sample collection period the GC column is stabilized at -50°C to allow for immediate injection of the sample after collection.

11.6 At the end of the collection period the valve is immediately placed in the inject position, and the cryogenic trap is rapidly heated to 120°C to desorb the components onto GC column. The GC temperature program and data acquisition are initiated at this time.

11.7 At the desired time the cryogenic trap is cooled to - 160°C, the valve is returned to the collect position and the next sample collection is initiated (to coincide with the completion of the GC analysis of the previous sample).

12. Calibration Procedure

Prior to sample analysis, and approximately every 4-6 hours thereafter, a calibration standard must be analyzed, using the identical procedure employed for ambient air samples (either Section 10 or 11). This section describes three alternative approaches for preparing suitable standards.

12.1 Teflon® (on Tedlar®) Bags

12.1.1 The bag (nominal size; 20L) is filled with zero air and leaked checked. This can be easily accomplished by placing a moderate weight (text book) on the inflated bag and leaving overnight. No visible change in bag volume indicates a good seal. The bag should also be equipped with a quick-connect fitting for sample withdrawal and an insertion port for liquid injections (Figure 2).

12.1.2 Before preparing a standard mixture, the bag is sequentially filled and evacuated with zero air (5 times). After the 5th filling, a sample blank is obtained using the sampling procedure outlined in Section 10.

12.1.3 In order to prepare a standard mixture, the bag is filled with a known volume of zero air. This flow should be measured via a calibrated mass flow controller or equivalent flow measuring device. A measured aliquot of each analyte of interest is injected into the bag through the insertion port using a microliter syringe. For those compounds with vapor pressures lower than benzene or for strongly adsorbed species, the bag should be heated (60°C) oven) during the entire calibration period.

12.1.4 To withdraw a sample for analysis, the sampling line is directly connected to the bag. Quick connect fittings allow this hook-up to be easily accomplished and also minimizes bag contamination from laboratory air. Sample collection is initiated as described earlier.

12.2 Glass Flasks

12.2.1 If a glass flask is employed (Figure 2) the exact volume is determined by weighing the flask before and after filling with deionized water. The flask is dried by heating at 200°C.

12.2.2 To prepare a standard, the dried flask is flushed with zero air until cleaned (i.e. a blank run is made). An appropriate aliquot of each analyte is injected using the same procedures as described for preparing bag standards.

12.2.3 To withdraw a standard for analysis, the GC sampling line is directly connected to the flask and a sample obtained. However, because the flask is a rigid container, it will not remain at atmospheric pressure after sampling has commenced. In order to prevent room air leakage into the flask, it is recommended that no more than 10% of the initial volume be exhausted during the calibration period (i.e. 200 cc if a 2 liter flask is used).

12.3 Pressurized Gas Cylinders

12.3.1 Pressurized gas cylinders containing selected analytes at ppb concentrations in air can be prepared or purchased. A limited number of analytes (e.g. benzene, propane) are available from NBS.

12.3.2 Speciality gas suppliers will prepare custom gas mixtures, and will cross reference the analyte concentrations to an NBS standard for an additional charge. In general, the user should purchase such custom mixtures, rather than attempting to prepare them because of the special high pressure filling apparatus required. However, the concentrations should be checked, either by the supplier or the user using NBS reference materials.

12.3.3 Generally, aluminum cylinders are suitable since most analytes of potential interest in this method have been shown to be stable for at least several months in such cylinders. Regulators constructed of stainless steel and Teflon® (no silicon or neoprene rubber).

12.3.4 Before use the tank regulator should be flushed by alternately pressuring with the tank mixture, closing the tank valve, and venting the regulator contents to the atmosphere several times.

12.3.5 For calibration a continuous flow of the gas mixture should be maintained through a glass or Teflon® manifold from which the calibration standard is drawn. To generate various calibration concentrations the pressurized gas mixture can be diluted, as desired, with zero grade air using a dynamic dilution system (e.g. CSI Model 1700).

13. Calibration Strategy

13.1 Vapor phase standards can be prepared with either neat liquids or diluted liquid mixtures depending upon the concentration levels desired. It is recommended that benzene, also be included in this preparation scheme so that flame ionization detector response factors, relative to benzene, can be determined for the other compounds. The benzene concentration generated in this fashion should be cross-checked with an NBS (e.g. SRM 1805) for accuracy determinations.

13.2 Under normal conditions, weekly multipoint calibrations should be conducted. Each multipoint calibration should include a blank run and four concentration levels for the target species. The generated concentrations should bracket the expected concentration of ambient air samples.

13.3 A plot of nanograms injected versus area using a linear least squares fit of the calibration data will yield the following equation:

$$Y = A + BX$$

where

Y = quantity of component, nanograms
A = intercept
B = slope (response factor)

If substantial nonlinearity is present in the calibration curve a quadratic fit of the data can be used:

$$Y = A + BX + CX^2$$

where

C = constant

Alternatively, a, stepwise multilevel calibration scheme may be used if more convenient for the data system in use.

14. Performance Criteria and Quality Assurance

This section summarizes the quality assurance (QA) measures and provides guidance concerning performance criteria which should be achieved within each laboratory.

14.1 Standard Operating Procedures (SOPs)

14.1.1 Each user should generate SOPs describing the following activities as accomplished in their laboratories:

1) assembly, calibration and operation of the sampling system.
2) preparation and handling of calibration standards.
3) assembly, calibration and operation of the GC/FID system and
4) all aspects of data recording and processing.

14.1.2 SOPs should provide specific stepwise instructions and should be readily available to, and understood by, the laboratory personnel conducting the work.

14.2 Method Sensitivity, Precision and Accuracy

14.2.1 System sensitivity (detection limit) for each component is calculated from the data obtained for calibration standards. The detection limit is defined as

$$DL = A + 3.3S$$

where

DL = calculated detection limit in nanograms injected.
A = intercept calculated in Section 13.
S = standard deviation of replicate determination of the lowest level standard (at least three determinations are required).

For many compounds detection limits of 1 to 5 nanograms are found using the flame ionization detection. Lower detection limits can be obtained for chlorinated hydrocarbons using the electron capture detector.

14.2.2 A precision of ± 5% (relative standard deviation) can be readily achieved at concentrations 10 times the detection limit. Typical performance data are included in Table 1.

14.2.3 Method accuracy is estimated to be within ± 10%, based on National Bureau of Standard calibrated mixtures.

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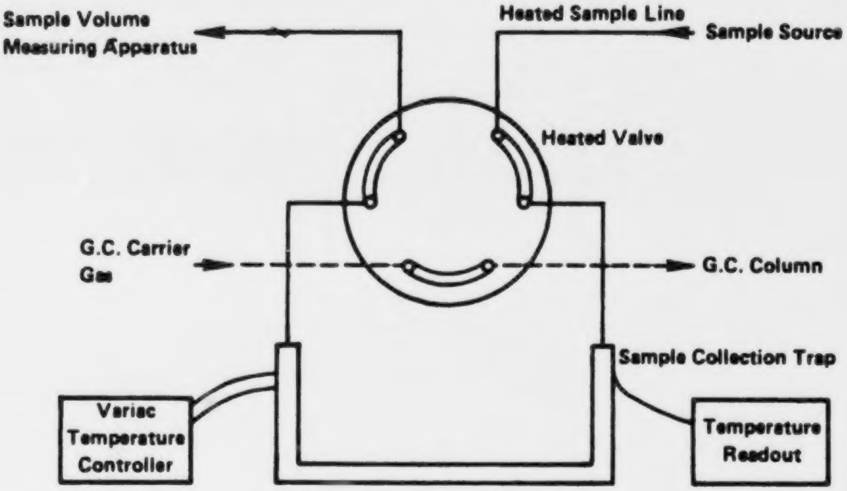
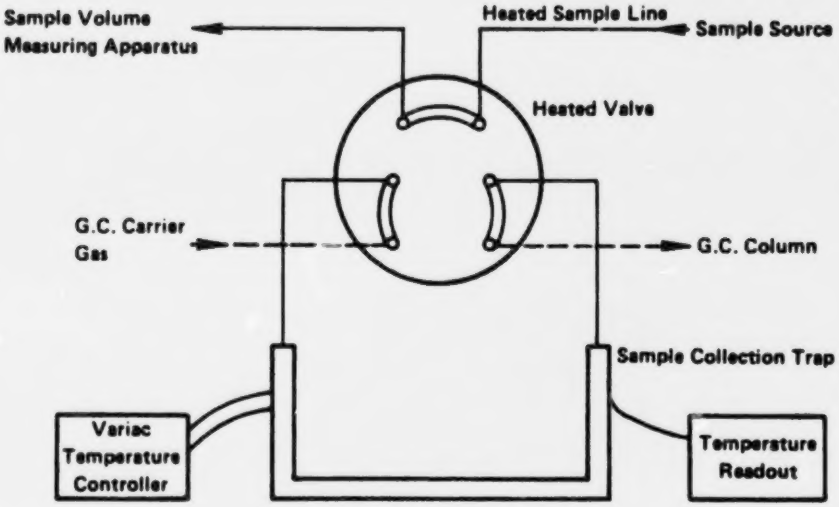

Sample Volume
Measuring Apparatus
Heated Sample Line
Sample Source
Heated Valve
G.C. Carrier
Gas
G.C. Column
Sample Collection Trap
Variac
Temperature
Controller
Temperature
Readout

a. Fill Position


Sample Volume
Measuring Apparatus
Heated Sample Line
Sample Source
Heated Valve
G.C. Carrier
Gas
G.C. Column
Sample Collection Trap
Variac
Temperature
Controller
Temperature
Readout

b. Injection Position

Figure 1. Schematic of Six-Port Valve Used for Sample Collection.

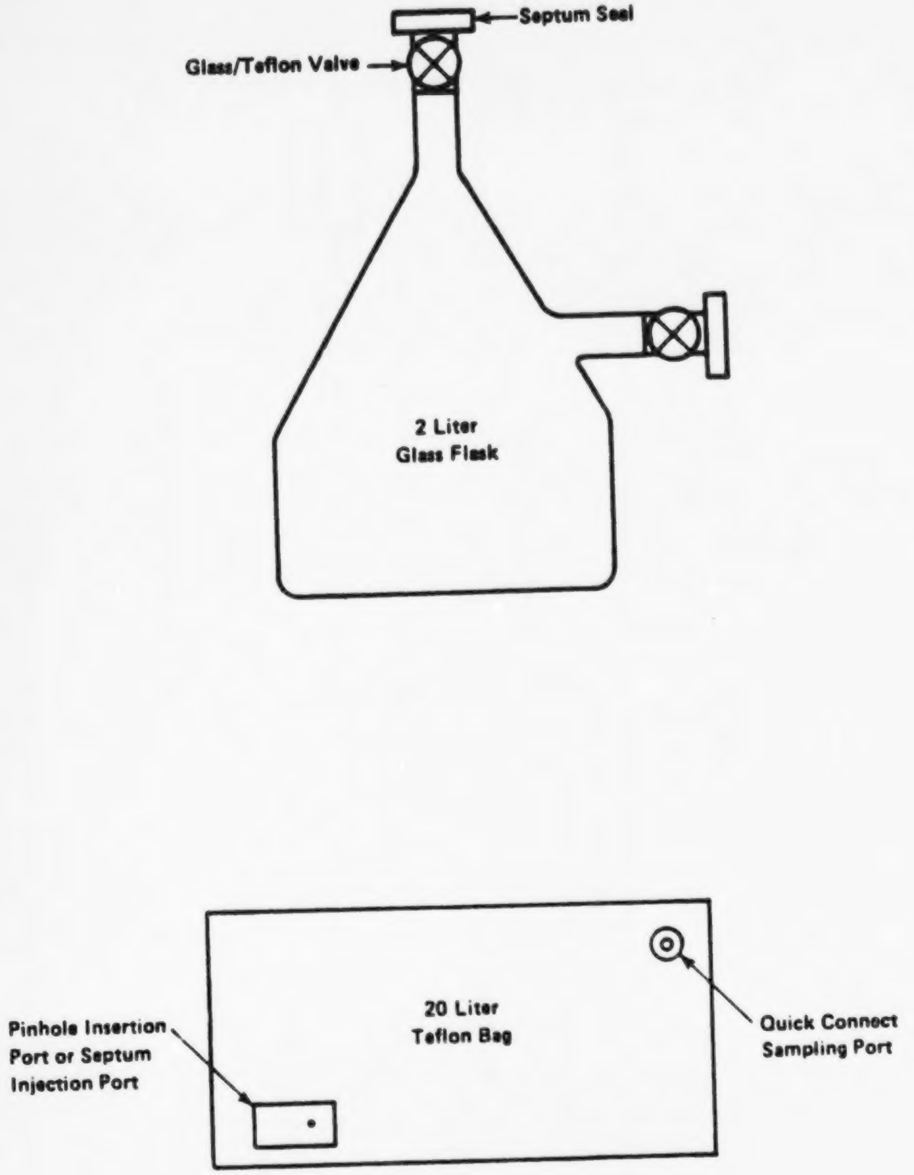

Septum Seal
Glass/Teflon Valve
2 Liter
Glass Flask
20 Liter
Teflon Bag
Pinhole Insertion
Port or Septum
Injection Port
Quick Connect
Sampling Port

Figure 2. Dilution Containers for Standard Mixtures

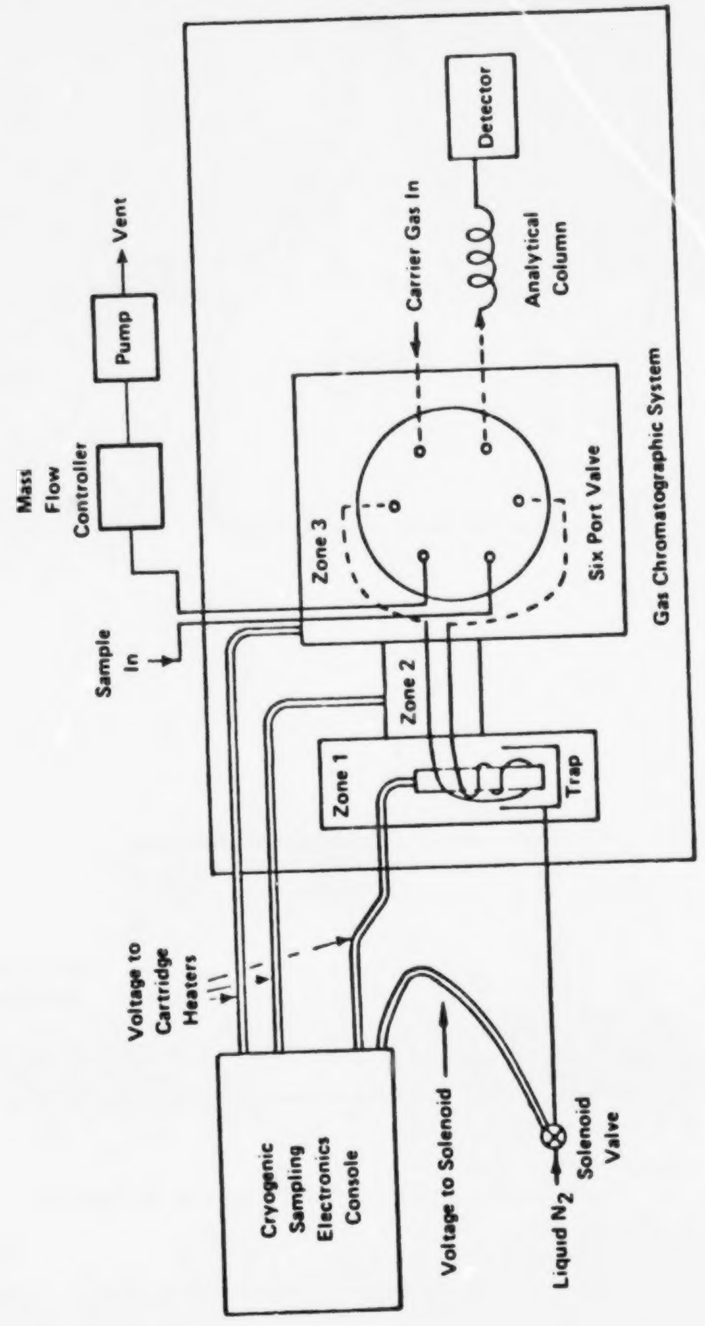
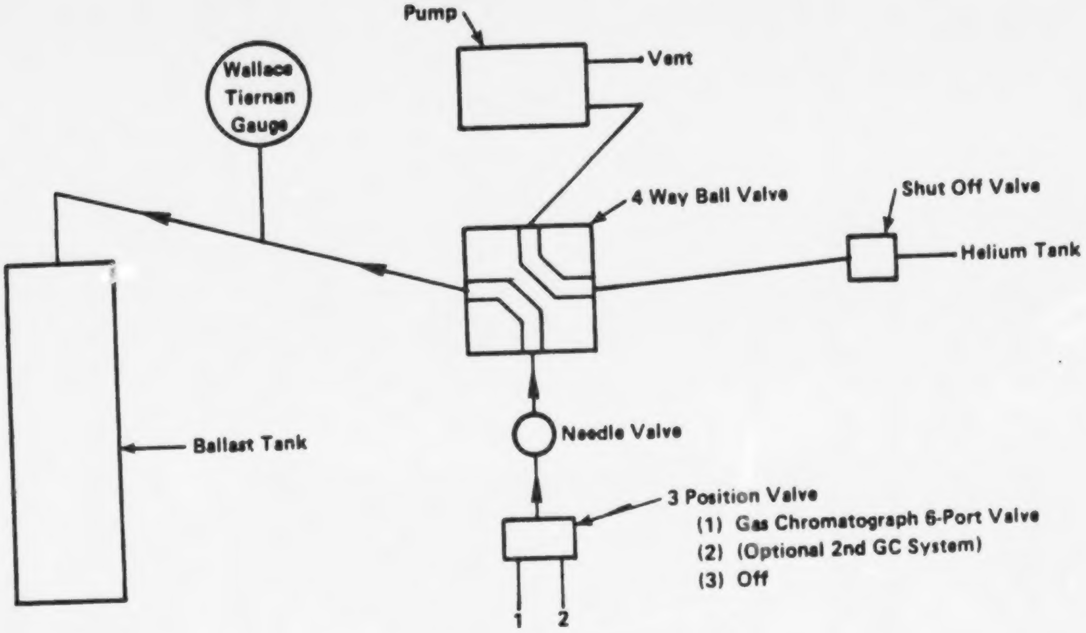
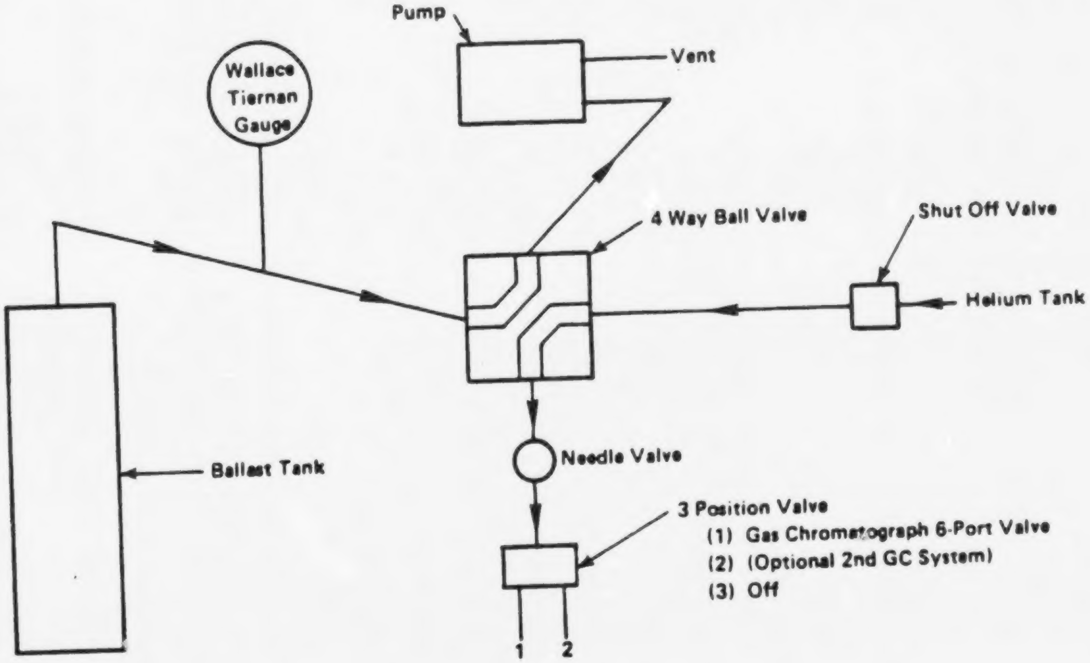

Cryogenic Sampling Electronics Console
Voltage to Cartridge Heaters
Voltage to Solenoid
Liquid N_2
Solenoid Valve
Sample In
Mass Flow Controller
Pump
Vent
Zone 1
Zone 2
Zone 3
Trap
Six Port Valve
Carrier Gas In
Analytical Column
Detector
Gas Chromatographic System

FIGURE 3. AUTOMATED SAMPLING AND ANALYSIS SYSTEM FOR CRYOGENIC TRAPPING


Pump
Vent
Wallace Tiernan Gauge
4 Way Ball Valve
Shut Off Valve
Helium Tank
Needle Valve
Ballast Tank
3 Position Valve
(1) Gas Chromatograph 6-Port Valve
(2) (Optional 2nd GC System)
(3) Off
1
2

(a) Volume Measuring Position


Pump
Vent
Wallace Tiernan Gauge
4 Way Ball Valve
Shut Off Valve
Helium Tank
Needle Valve
Ballast Tank
3 Position Valve
(1) Gas Chromatograph 6-Port Valve
(2) (Optional 2nd GC System)
(3) Off
1
2

(b) Pump – Down Position

Figure 4. Sample Volume Measuring Apparatus

TABLE 1. VOLATILE ORGANIC COMPOUNDS FOR WHICH THE CRYOGENIC SAMPLING METHOD HAS BEEN EVALUATED[(a)]

Compound	Retention Time, Minutes[(b)]	Test 1 (4 runs, 200cc samples)		Test 2 (8 runs, 200-cc samples)	
		Mean (ppb)	%RSD	Mean (ppb)	%RSD
Vinylidene Chloride	9.26	144	4.4	6.1	3.9
Chloroform	12.16	84	3.8	3.5	5.8
1,2-Dichloroethane	12.80	44	3.7	1.9	5.1
Methylchloroform	13.00	63	4.5	2.7	4.9
Benzene	13.41	93	4.0	3.9	5.1
Trichloroethylene	14.48	84	3.7	3.5	4.1
Tetrachloroethylene	17.37	69	3.7	2.9	4.3
Chlorobenzene	18.09	46	3.3	1.9	3.2

a)Recovery efficiencies were 100 ± 5% as determined by comparing direct sample loop (5cc) injections with cryogenic collection techniques (using test 1 data). Data from reference 10.

b)GC conditions as follows:

Column - Hewlett Packard, crosslinked methyl silicone, 0.32 mm ID x 50 m long, thick film, fused silica.

Temperature Program - 50°C for 2 minutes, then increased at 8°C/minute to 150°C.

METHOD FOR THE DETERMINATION OF ORGANOCHLORINE PESTICIDES AND POLYCHLORINATED BIPHENYLS IN AMBIENT AIR

1. Scope

1.1 This document describes a method for determination of a variety of organochlorine pesticides and polychlorinated biphenyls (PCBs) in ambient air. Generally, detection limits of >1 ng/m^3 are achievable using a 24-hour sampling period.

1.2 Specific compounds for which the method has been employed are listed in Table 1. Several references are available which provide further details on the development and application of the method. The sample cleanup and analysis methods are identical to those described in U. S. EPA Method 608. That method is included as Appendix A of this methods compendium.

2. Applicable Documents

2.1 ASTM Standards
D1356 Definition of Terms Related to Atmospheric Sampling and Analysis (7).

2.2 Other Documents
Ambient Air Studies (1-3)
U. S. EPA Technical Assistance Document (4).
U. S. EPA Method 608 (5). See Appendix A of methods compendium.

3. Summary of Method

3.1 A modified high volume sampler consisting of a glass fiber filter with a polyurethane foam (PUF) backup absorbent cartridge is used to sample ambient air at a rate of $\sim$200-280 L/minute.

3.2 The filter and PUF cartridge are placed in clean, sealed containers and returned to the laboratory for analysis. The PCBs and pesticides are recovered by Soxhlet extraction with 5% ether in hexane.

3.3 The extracts are reduced in volume using Kuderna-Danish (K-D) concentration techniques and subjected to column chromatographic cleanup.

3.4 The extracts are analyzed for pesticides and PCBs using gas chromatography with electron capture detection (GC-ECD), as described in U. S. EPA Method 608 (5).

4. Significance

4.1 Pesticides, particularly organochlorine pesticides, are widely used in both rural and urban areas for a variety of applications. PCBs are less widely used, due to extensive restrictions placed on their manufacture. However, human exposure to PCBs continues to be a problem because of their presence in various electrical products.

4.2 Many pesticides and PCBs exhibit bioaccumulative, chronic health effects and hence monitoring ambient air for such compounds is of great importance.

4.3 The relatively low levels of such compounds in the environment requires the use of high volume sampling techniques to acquire sufficient sample for analysis. However, the volatility of these compounds prevents efficient collection on filter media. Consequently, this method utilizes both a filter and a PUF backup cartridge which provides for efficient collection of most organochlorine pesticides, PCBs, and many other organics within the same volatility range.

5. Definitions

Definitions used in this document and any user-prepared SOPs should be consistent with ASTM D1356 (7). All abbreviations and symbols are defined within this document at the point of use.

6. Interferences

6.1 The use of column chromatographic cleanup and selective GC detection (GC-ECD) minimizes the risk of interference from extraneous organic compounds. However, the fact that PCBs as well as certain organochlorine pesticides (e.g. toxaphene and chlordane) are complex mixtures of individual compounds can cause difficulty in accurately quantifying a particular formulation in a multiple component mixture.

6.2 Contamination of glassware and sampling apparatus with traces of pesticides or PCBs can be a major source of error in the method, particularly when sampling near high level sources (e.g. dumpsites, waste processing plants, etc.) careful attention to cleaning and handling procedures is required in all steps of the sampling and analysis to minimize this source of error.

7. Apparatus

7.1 Hi-Vol Sampler with PUF cartridge - available from General Metal Works (Model PS-1). See Figure 1.

7.2 Sampling Head to contain glass cartridge with PUF plug - available from General Metal Works. See Figure 2.

7.3 Calibration orifice - available from General Metal Works.

7.4 Manometer - to use with calibration orifice.

7.5 Soxhlet extraction system - including Soxhlet extractors (500 and 250 mL), heating mantels, variable voltage transformers, and cooling water source - for extraction of PUF cartridges before and after sampling. Also for extraction of filter samples.

7.6 Vacuum oven connected to water aspirator - for drying extracted PUF cartridges.

7.7 Gas chromatograph with electron capture detector - (consult U. S. EPA Method 608 for specifications).

7.8 Forceps - to handle quartz fiber filter samples.

7.9 Die - to cut PUF plugs.

7.10 Various items for extract preparation, cleanup, and analysis - consult U. S. EPA Method 608 for detailed listing.

7.11 Chromatography column - 2 mm I.D. x 15 cm long - for alumina cleanup.

8. Reagent and Materials

8.1 Polyurethane foam - 3 inch thick sheet stock, polyether type used in furniture upholstering. Density 0.022 g/cm^3.

8.2 Polyester gloves - for handling PUF cartridges and filters

8.3 Filters, quartz fiber - Pallflex 2500 QAST , or equivalent.

8.4 Wool felt filter - 4.9 mg/cm^2 and 0.6 mm thick. To fit sample head for collection efficiency studies. Pre-extracted with 5% diethyl ether in hexane.

8.5 Hexane - Pesticide or distilled in glass grade.

8.6 Diethyl ether - preserved with 2% ethanol - distilled in glass grade, or equivalent.

8.7 Acetone - Pesticide or distilled in glass grade,

8.8 Glass container for PUF cartridges.

8.9 Glass petri dish - for shipment of filters to and from the laboratory.

8.10 Ice chest - to store samples at ∿0°C after collection.

8.11 Various materials needed for extract preparation, cleanup, and analysis - consult U. S. EPA Method 608 for details (Appendix A of this compendium).

8.12 Alumina - activity grade IV. 100/200 mesh

9. Assembly and Calibration of Sampling Apparatus

9.1 Description of Sampling Apparatus

9.1.1 The entire sampling system is diagrammed in Figure 1. This sampler was developed by Syracuse University

Research Corporation (SURC) under a U. S. EPA contract (6) and further modified by Southwest Research Institute and the U. S. EPA. A unit specifically designed for this method is now commercially available (Model PS-1 - General Metal Works, Inc., Village of Cleves, Ohio). The method writeup assumes the use of the commercial device, although the earlier modified device is also considered acceptable.

9.1.2 The sampling module (Figure 2) consists of a glass sampling cartridge and an air-tight metal cartridge holder. The PUF plug is retained in the glass sampling cartridge.

9.2 Calibration of Sampling System

9.2.1 The airflow through the sampling system is monitored by a venturi/Manehelic assembly, as shown in Figure 1. A multipoint calibration of the venturi/magnehelic assembly must be conducted every six months using an audit calibration orifice, as described in the U. S. EPA High Volume Sampling Method (8). A single point calibration must be performed before and after each sample collection, using the procedure described below.

9.2.2 Prior to calibration a "dummy" PUF cartridge and filter are placed in the sampling head and the sampling motor is activated. The flow control valve is fully opened and the voltage variator is adjusted so that a sample flow rate corresponding to ∿110% of the desired flow rate is indicated on the magnehelic (based on the previously obtained multipoint calibration curve). The motor is allowed to warmup for ∿10 minutes and then the flow control valve is adjusted to achieve the desired flow rate. The ambient temperature and barometric pressure should be recorded on an appropriate data sheet (e.g. Figure 3).

9.2.3 The calibration orifice is then placed on the sampling head and a manometer is attached to the tap on the calibration orifice. The sampler is momentarily turned off to set the zero level of the manometer. The sampler is then switched on and the manometer reading is recorded, once a stable reading is achieved. The sampler is then shut off.

9.2.4 The calibration curve for the orifice is used to calculate sample flow from the data obtained in 9.2.3, and the calibration curve for the venturi/magnehelic assembly is used to calculate sample flow from the data obtained in 9.2.2. The calibration data should be recorded on an appropriate data sheet (e.g. Figure 3). If the two values do not agree within 10% the sampler should be inspected for damage, flow blockage, etc. If no obvious problems are found the sampler should be recalibrated (multipoint) according to the U. S. EPA High Volume Sampling procedure (8).

9.2.5 A multipoint calibration of the calibration orifice, against a primary standard, should be obtained annually.

10. Preparation of Sampling (PUF) Cartridges

10.1 The PUF adsorbent is a polyether-type polyurethane foam (density No. 3014 or 0.0225 g/cm^3). This type of foam is used for furniture upholstery. It is white and yellows on exposure to light.

10.2 The PUF inserts are 6.0 cm diameter cylindrical plugs cut from 3 inch sheet stock and should fit with slight compression in the glass cartridge, supported by the wire screen. See Figure 2. During cutting the die is rotated at high speed (e.g. in a drill press) and continuously lubricated with water.

10.3 For initial cleanup the PUF plug is placed in a Soxhlet extractor and extracted with acetone for 14-24 hours at approximately 4 cycles per hour. When cartridges are reused, 5% diethyl ether in n-hexane can be used as the cleanup solvent.

10.4 The extracted PUF is placed in a vacuum oven connected to a water aspirator and dried at room temperature for approximately 2-4 hours (until no solvent odor is detected).

10.5 The PUF is placed into the glass sampling cartridge using polyester gloves. The module is wrapped with hexane rinsed aluminum foil, placed in a labeled container and tightly sealed.

10.6 Other adsorbents may be suitable for this method as indicated in the various references (1-3). If such materials are employed the user must define appropriate preparation procedures based on the information contained in these references.

10.7 At least one assembled cartridge from each batch must be analyzed, as a laboratory blank, using the procedures described in Section 12, before the batch is considered acceptable for field use. A blank level of <10 ng/plug for single compounds is considered to be acceptable. For multiple component mixtures (e.g. Arochlors) the blank level should be <100 ng/plug.

11. Sampling

11.1 After the sampling system has been assembled and calibrated as described in Section 9 it can be used to collect air samples as described below.

11.2 The samples should be located in an unobstructed area, at least two meters from any obstacle to air flow. The exhaust hose should be stretched out in the downwind direction to prevent recycling of air.

11.3 A clean sampling cartridge and quartz fiber filter are removed from sealed transport containers and placed in the sampling head using forceps and gloved hands. The head is tightly sealed into the sampling system. The aluminum foil wrapping is placed back in the sealed container for later use.

11.4 The zero reading of the Magnehelic is checked. Ambient temperature, barometric pressure, elapsed time meter setting, sampler serial number, filter number and PUF cartridge number are recorded. A suitable data sheet is shown in Figure 4.

11.5 The voltage variator and flow control valve are placed at the settings used in 9.2.3 and the power switch is turned on. The elapsed time meter is activated and the start time recorded. The flow (Magnehelic setting) is adjusted, if necessary using the flow control valve.

11.6 The Magnehelic reading is recorded every six hours during the sampling period. The calibration curve (Section 9.2.7) is used to calculate the flow rate. Ambient temperature and barometric pressure are recorded at the beginning and end of the sampling period.

11.7 At the end of the desired sampling period the power is turned off and the filter and PUF cartridges are wrapped with the original aluminum foil and placed in sealed, labeled containers for transport back to the laboratory.

11.8 The Magnehelic calibration is checked using the calibration orifice as described in Section 9.2.4. If the calibration deviates by more than 10% from the initial reading the flow data for that sample must be marked as suspect and the sampler should be inspected and/or removed from service.

11.9 At least one field blank will be returned to the laboratory with each group of samples. A field blank is treated exactly as a sample except that no air is drawn through the cartridge.

11.10 Samples are stored at ∿20°C in an ice chest until receipt at the analytical laboratory, at which time they are stored refrigerated at 4°C.

12. Sample Preparation and Analysis

12.1 Sample Preparation

12.1.1 All samples should be extracted within 1 week after collection.

12.1.2 PUF cartridges are removed from the sealed con-container using gloved hands, the aluminum foil wrapping is removed, and the cartridges are placed into a 500-mL Soxhlet extraction. The cartridges are extracted for 14-24 hours at ∿4 cycles/hour with 5% diethyl ether in hexane. Extracted cartridges can be dried and reused following the handling procedures in Section 10. The quartz filter can be placed in the extractor with the PUF cartridges. However, if separate analysis is desired then one can proceed with 12.1.3.

12.1.3 If separate analysis is desired, quartz filters are placed in a 250-mL Soxhlet extractor and extracted for 14-24 hours with 5% diethyl ether in hexane.

12.1.4 The extracts are concentrated to 10 mL final volume using 500-mL Kuderna-Danish concentrators as described in EPA Method 608 (5), using a hot water bath. The concentrated extracts are stored refrigerated in sealed 4-dram vials having teflon-lined screw-caps until analyzed or subjected to cleanup.

12.2 Sample Cleanup

12.2.1 If only organochlorine pesticides and PCBs are sought, an alumina cleanup procedure reported in the literature is appropriate (1). Prior to cleanup the sample extract is carefully reduced to 1 mL using a gentle steam of clean nitrogen.

12.2.2 A glass chromatographic column (2 mm ID x 15 cm long) is packed with alumina, activity grade IV and rinsed with ∿20 mL of n-hexane. The concentrated sample extract (from 12.2.1) is placed on the column and eluted with 10 mL of n-hexane at a rate of 0.5 mL/minute. The eluate volume is adjusted to exactly 10 mL and analyzed as described in 12.3.

12.2.3 If other pesticides are sought, alternate cleanup procedures (e.g. Florisil) may be required. Method 608 (5) identifies appropriate cleanup procedures.

12.3 Sample Analysis

12.3.1 Sample analysis is performed using GC/ECD as described in EPA Method 608 (5). The user must consult this method for detailed analytical procedures.

12.3.2 GC retention times and conditions are identified in Table 1 for the compounds of interest.

13. GC Calibration

Appropriate calibration procedures are identified in EPA Method 608 (5).

14. Calculations

14.1 The total sample volume (V_m) is calculated from the periodic flow readings (Magnehelic) taken in Section 11.6 using the following equation.

$$V_m = \frac{Q_1 + Q_2 \cdots Q_N}{N} \times \frac{T}{1000}$$

where

V_m = Total sample volume (m^3).

$Q_1, Q_2 \ldots Q_N$ = Flow rates determined at the beginning, end, and intermediate points during sampling (L/minute).

N = Number of data points averaged.

T = Elapsed sampling time (minutes).

14.2 The volume of air sampled can be converted to standard conditions (760 mm Hg pressure and 25°C) using the following equation:

$$V_s = V_m \times \frac{P_A}{760} \times \frac{298}{273+t_A}$$

where

V_s = Total sample volume at 25°C and 760 mm Hg pressure (m^3)

V_m = Total sample flow under ambient conditions (m^3)

P_A = Ambient pressure (mm Hg)

t_A = Ambient temperature (°C)

14.3 The concentration of compound in the sample is calculated using the following equation:

$$C_A = \frac{A \times V_E}{V_i \times V_s}$$

where

C_A = Concentration of analyte in the sample, $\mu g/m^3$

A = Calculated amount of material injected onto the chromatograph based on calibration curve for injected standards (nanograms)

V_i = Volume of extract injected (μL).

V_E = Final volume of extract (mL).
V_s = Total volume of air samples corrected to standard conditions (m^3).

14. Performance Criteria and Quality Assurance

This section summarizes the quality assurance (QA) measures and provides guidance concerning performance criteria which should be achieved within each laboratory.

14.1 Standard Operating Procedures (SOPs)

14.1.1 Users should generate SOPs describing the following activities as accomplished in their laboratory: 1) assembly, calibration and operation of the sampling system, 2) preparation, purification, storage and handling of sampling cartridges, 3) assembly, calibration and operation of the GC/ECD system, and 4) all aspects of data recording and processing.

14.1.2 SOPs should provide specific stepwise instructions and should be readily available to, and understood by, the laboratory personnel conducting the work.

14.2 Process, Field, and Solvent Blanks

14.2.1 One PUF cartridge and filter from each batch of approximately twenty should be analyzed, without shipment to the field, for the compounds of interest to serve as a process blank.

14.2.2 During each sampling episode at least one PUF cartridge and filter should be shipped to the field and returned, without drawing air through the sampler, to serve as a field blank.

14.2.3 During the analysis of each batch of samples at least one solvent process blank (all steps conducted but no PUF cartridge or filter included) should be carried through the procedure and analyzed.

14.2.4 Blank levels should not exceed ∿10 ng/sample for single components or ∿100 ng/sample for multiple component mixtures (e.g. PCBs).

14.3 Collection Efficiency and Spike Recovery

14.3.1 Before using the method for sample analysis each laboratory must determine their collection efficiency for the components of interest.

14.3.2 The glass fiber filter in the sampler is replaced with a hexane-extracted wool felt filter (weight 14.9 mg/cm^2, 0.6 mm thick). The filter is spiked with microgram amounts of the compounds of interest by dropwise addition of hexane solutions of the compounds. The solvent is allowed to evaporate and filter is placed into the sampling system for immediate use.

14.3.3 The sampling system, including a clean PUF cartridge , is activated and set at the desired sampling flow rate. The sample flow is monitored for 24 hours.

14.3.4 The filter and PUF cartridge are then removed and analyzed as described in Section 12.

14.3.5 A second sample, unspiked is collected over the same time period to account for any background levels of components in the ambient air matrix.

14.3.6 A third PUF cartridge is spiked with the same amounts of the compounds used in 14.3.2 and extracted to determine analytical recovery.

14.3.7 In general analytical recoveries and collection efficiencies of 75% are considered to be acceptable method performance.

14.3.8 Replicate (at least triplicate) determinations of collection efficiency should be made. Relative standard deviations for these replicate determinations of ± 15% or less is considered acceptable performance.

14.3.9 Blind spiked samples should be included with sample sets periodically, as a check on analytical performance.

14.4 Method Precision and Accuracy

Typical method recovery data are shown in Table 1. Recoveries for the various chlorobiphenyls illustrate the fact that all components of an Arochlor mixture will not be retained to the same extent. Recoveries for tetrachlorobiphenyls and above are generally greater than 85% but di- and trichloro homologs may not be recovered quantitatively.

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TABLE 1. SELECTED COMPONENTS DETERMINED USING HI-VOL/PUF SAMPLING PROCEDURE

		24-Hour Sampling Efficiency(b)	
Compound	GC Retention Time, Minutes(a)	Air Concentration ng/m^3	% Recovery
Aldrin	2.4	0.3-3.0	28
4,4'-DDE	5.1	0.6-6.0	89
4,4'-DDT	9.4	1.8-18	83
Chlordane	(c)	15-150	73
Chlorobiphenyls			
4,4' Di-	--	2.0-20	62
2,4,5 Tri-	---	0.2-2.0	36
2,4',5 Tri-	--	0.2-2.0	86
2,2',5,5' Tetra-	--	0.2-2.0	94
2,2',4,5,5' Penta-	--	0.2-2.0	92
2,2',4,4',5,5' Hexa	--	0.2-2.0	86

(a) Data from U.S. EPA Method 608. Conditions are as follows:

Stationary Phase - 1.5% SP2250/1.95% SP-2401 on Supelcoport (100/120 mesh) packed in 1.8 mm long x 4 mm ID glass column.

Carrier - 5/95 methane/Argon at 60 mL/Minute

Column Temperature - 160°C except for PCBs which are determined at 200°C.

(b) From Reference 2.

(c) Multiple component formulation. See U.S. EPA Method 608.

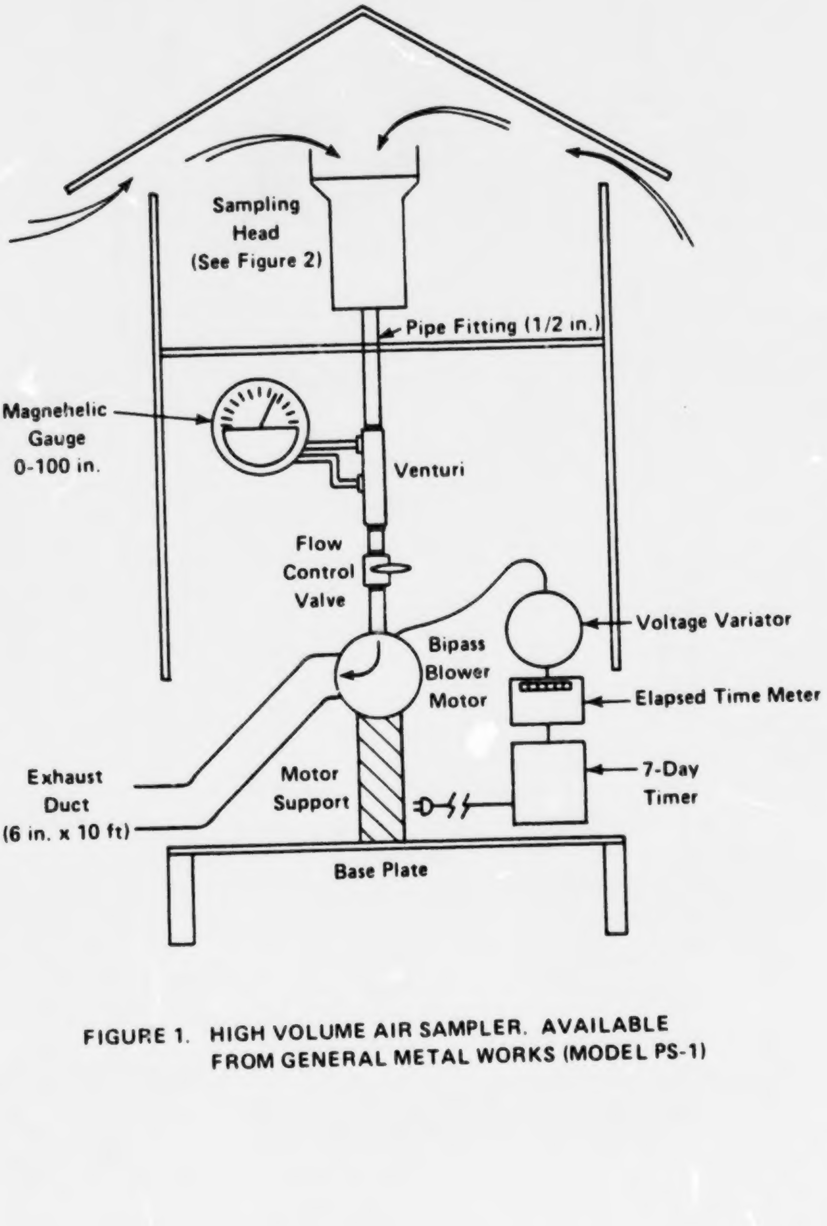

Sampling
Head
(See Figure 2)
Pipe Fitting (1/2 in.)
Magnehelic
Gauge
0-100 in.
Venturi
Flow
Control
Valve
Voltage Variator
Bipass
Blower
Motor
Elapsed Time Meter
7-Day
Timer
Exhaust
Duct
(6 in. x 10 ft)
Motor
Support
Base Plate

FIGURE 1. HIGH VOLUME AIR SAMPLER. AVAILABLE FROM GENERAL METAL WORKS (MODEL PS-1)

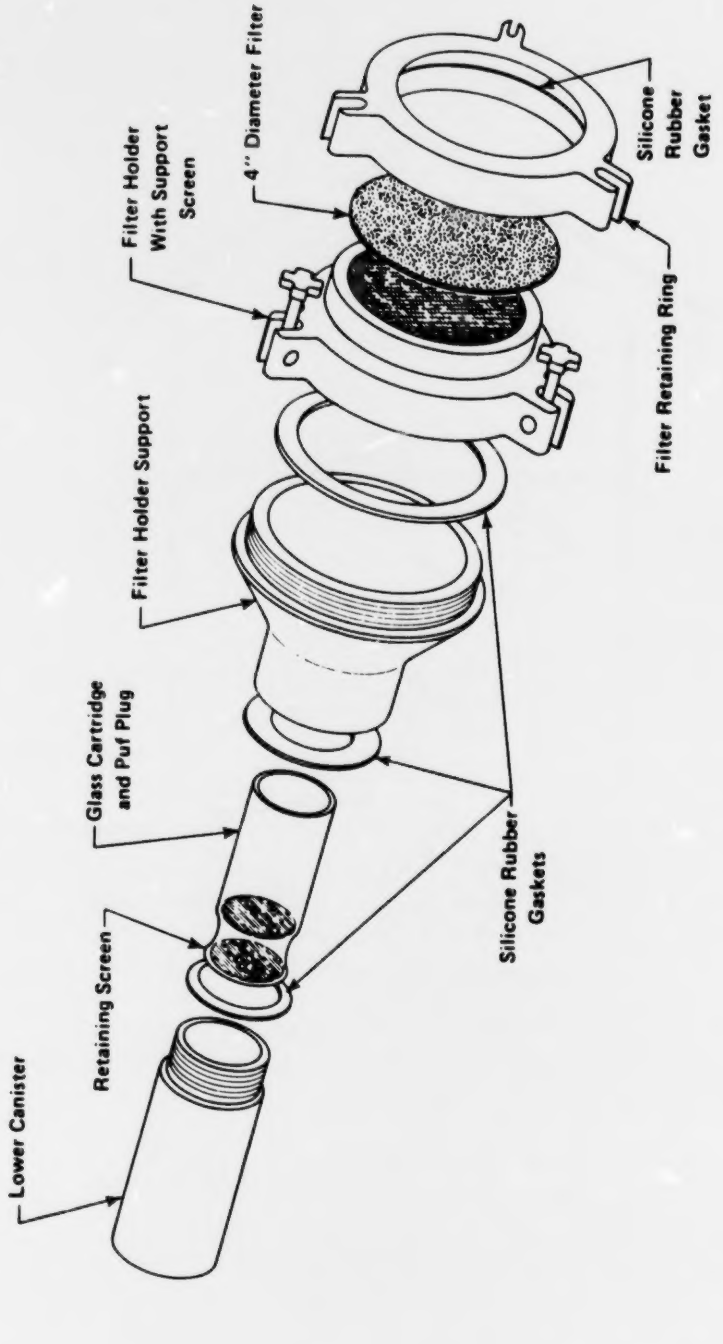

Lower Canister
Retaining Screen
Glass Cartridge and Puf Plug
Silicone Rubber Gaskets
Filter Holder Support
Filter Holder With Support Screen
4'' Diameter Filter
Filter Retaining Ring
Silicone Rubber Gasket

FIGURE 2. SAMPLING HEAD

Performed by____________ Calibration Orifice S/N____________ Ambient Temperature________°C

Date/Time____________ Manometer S/N ____________ Bar.Press. ________ mm Hg

Sampler S/N	Variac Setting V	Timer OK? Yes/No	Calibration Orifice Data		Sampler Venturi Data		% Difference Between Calibration and Sample Venturi Flow Rates	Comments
			Manometer, in. H_2O	Flow Rate, scm /min[a]	Magnehelic, in. H_2O	Flow Rate scm/min [b]		

(a) From Calibration Tables for Calibration Orifice or Venturi Tube

(b) From Calibration Tables for Venturi Tube in each Hi-Vol unit.

Date check by____________ Date____________

FIGURE 3. TYPICAL CALIBRATION SHEET FOR HIGH VOLUME SAMPLER

Site ______________________ Date ______________________ Performed by ______________________

Sampler S/N	Sampling Location I.D.	New Filter (√)	PUF Cart. No.	Variac Setting	Clock Time			Sampler Timer			Venturi Readings: Time/Magnehelic in. H_2O				Ambient Temperature, °C		Barometric Pressure, mm Hg		Comments
					Start, hr CDT	Stop, hr CDT	Min Elapsed	Start, min	Stop, min	Min Elapsed	1	2	3	4	Start	Stop	Start	Stop	

(a) Record any evidence of tampering with sampler and/or abnormalities in sampler operation, PUF cartridge condition or handling, etc.

Data Checked By ______________________ Date ______________

FIGURE 4. TYPICAL SAMPLING DATA FORM FOR HIGH VOLUME PESTICIDE/PCB SAMPLER

METHOD TO5 -1

Revision 1.0
April, 1984

METHOD FOR THE DETERMINATION OF ALDEHYDES AND KETONES IN AMBIENT AIR USING HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

1. Scope

1.1 This document describes a method for determination of individual aldehydes and ketones in ambient air. With careful attention to reagent purity and other factors the method can detect most monofunctional aldehydes and ketones at the 1-2 ppbv level.

1.2 Specific compounds for which the method has been employed are listed in Table 1. Several studies have used the same basic method, with minor procedural differences, for analysis of ambient air (1-3).

2. Applicable Documents

2.1 ASTM Standards:
D 1356 Definitions of Terms Related to Atmospheric Sampling and Analysis (s)

2.2 Other Documents
Ambient air studies (1-3).
U.S. EPA Technical Assistance Document (4)

3. Summary of Method

3.1 Ambient air is drawn through a midget impinger containing 10 mL of 2N HCl/0.05% 2,4-dinitrophenylhydrazine (DNPH reagent) and 10 mL of isooctane. Aldehydes and ketones readily form stable 2,4-dinitrophenylhydrazones (DNPH derivatives).

3.2 The impinger solution is placed in a screw-capped vial having a teflon-lined cap and returned to the laboratory for analysis. The DNPH derivatives are recovered by removing the isooctane layer, extracting the aqueous layer with 10 mL of 70/30 hexane/methylene chloride, and combining the organic layers.

3.3 The combined organic layers are evaporated to dryness under a steam of nitrogen and the residue dissolved in methanol.

3.4 The DNPH derivatives are determined using reversed phase HPLC with an ultraviolet (UV) adsorption detector operated at 370 nm.

4. Significance

4.1 Aldehydes and ketones are emitted into the atmosphere from chemical operations and various combustion sources. In addition, several of these compounds (e.g. formaldehyde and acetaldehyde) are produced by photochemical degradation of other organic compounds. Many of these compounds are acutely toxic and/or carcinogenic, thus requiring their determination in ambient air in order to assess human health impacts.

4.2 Conventional methods for aldehydes and ketones have generally employed colorimetric techniques wherein only one or two compounds are detected, or the sum of numerous compounds is determined. The method described herein provides a means for specifically determining a wide variety of aldehydes and ketones at typical ambient concentrations.

5. Definitions

Definitions used in this document and any user prepared SOPs should be consistent with ASTM D1356(5). All abbreviations and symbols are defined within this document at the point of use.

6. Interferences

6.1 The only significant interferences in the method are certain isomeric aldehydes or ketones which may be unresolved by the HPLC system. Such interferences can often be overcome by altering the separation conditions (e.g. using alternate HPLC columns or mobile phase compositions).

6.2 Formaldehyde contamination of the DNPH reagent is a frequently encountered problem. The reagent must be prepared within 48 hours before use and must be stored in an uncontaminated environment before and after sampling to minimize blank problems. Acetone contamination is apparently unavoidable. Consequently, the method cannot be used to accurately measure acetone levels except in highly contaminated environments.

7. Apparatus

7.1 Isocratic HPLC system-consisting of high pressure pump, injection valve, Zorbax ODS column (25 cm x 4.6 mm ID), variable wavelength UV detector, and data system or stripchart recorded. See Figure 3.

7.2 Sampling system-capable of accurately and precisely sampling 100-1000 mL/minute of ambient air. See Figure 1.

7.3 Stopwatch

7.4 Friction top metal can e.g. one-gallon (paint can) - to hold DNPH reagent and samples

7.5 Thermometer - to record ambient temperature.

7.6 Barometer (optional)

7.7 Analytical balance - 0.1 mg sensitivity

7.8 Reciprocating shaker

7.9 Midget impingers - jet inlet type - 25 mL volume.

7.10 Ice bath - for cooling impingers during sampling.

7.11 Nitrogen evaporator with heating block - for concentrating samples

7.12 Suction filtration apparatus - for filtering HPLC mobile phase.

7.13 Volumetric flasks - 100 mL and 500 mL.

7.14 Pipettes - various sizes, 1-10 mL.

7.15 Helium purge line (optional) - for degassing HPLC mobile phase.

7.16 Erlenmeyer flask, 1-liter - for preparing HPLC mobile phase.

7.17 Graduated cylinder, 1 liter - for preparing HPLC mobile phase.

7.18 Microliter syringe, 10-25 µL - for HPLC injector.

8. Reagents and Materials

8.1 Bottles, 10 oz. glass, with teflon-lined screw cap - for storing DNPH reagent.

8.2 Vials, 50 mL, with teflon-lined screw cap - for holding samples and extracts.

8.3 Disposable pipettes and bulbs.

8.4 Granular charcoal.

8.5 Methanol, hexane, methylene chloride, isooctane - distilled in glass or pesticide grade.

8.6 2,4-Dinitrophenylhydrazine - highest purity available (20% moisture).

8.7 Nitrogen, compressed gas cylinder - 99.99% purity for sample evaporation.

8.8 Polyester filters, 0.22 µm - Nuclepore or equiv.

8.9 DNPH derivatives of the components of interest - synthesized from DNPH and neat aldehydes according to reference (7). Recrystallized from ethanol before use.

9. Preparation of DNPH Reagent

9.1 Each batch of DNPH reagent should be prepared and purified within 48 hours of sampling, according to the procedure described in this section.

9.2 Two hundred and fifty milligrams of solid 2,4-dinitrophenylhydrazine and 90 mL of concentrated hydrochloric acid are placed into a 500 mL volumetric flask and the flask is filled to the mark with reagent water. The flask is then inverted several times or sonified until all of the solid material has dissolved.

9.3 Approximately 400 mL of the DNPH reagent is placed in a 16 ounce glass screw-capped bottle having a teflon-lined cap. Approximately 50 mL of a 70/30 (V/V) hexane/methylene chloride mixture is added to the bottle and the capped bottle is shaken for 15 minutes on a reciprocating shaker. The organic layer is then removed and discarded by decanting as much as possible and using a disposable pipette to remove the remaining organic layer.

9.4 The DNPH reagent is extracted two more times as described in 9.3. The bottle is then tightly capped, sealed with teflon tape, and placed in a friction top can (paint can) containing a 1-2 inch layer of granulated charcoal. The bottle is kept in the sealed can prior to use.

9.5 A portion of the DNPH reagent is analyzed using the procedure described in Section 11 prior to use in order to ensure that adequate background levels are maintained.

10. Sampling

10.1 The sampling apparatus is assembled and should be similar to that shown in Figure 1. EPA Method 6 uses essentially the same sampling system (8). All glassware (e.g. impingers, sampling bottles, etc.) must be thoroughly rinsed with methanol and oven dried before use.

10.2 Prior to sample collection the entire assembly (including empty sample impingers) is installed and the flow rate checked at a value near the desired rate. In general flow rates of 100-1000 mL/minute are useful. Flow rates greater than ∿1000 mL/minute should not be used because impinger collection efficiency may decrease. Generally calibration is accomplished using a soap bubble flow meter or calibrated wet test meter connected to the flow exit, assuming the entire system is sealed. ASTM Method D3686 describes an appropriate calibration scheme not requiring a sealed flow system downstream of the pump.

10.3 Ideally a dry gas meter is included in the system to record total flow. If a dry gas meter is not available the operator must measure and record the sampling flow rate at the beginning and end of the sampling period to determine sample volume. If the sampling period exceeds two hours the flow rate should be measured at intermediate points during the sampling period. Ideally a rotameter should be included to allow observation of the flow rate without interruption of the sampling process.

10.4 To collect an air sample two clean midget impingers are loaded with 10 mL of purified DNPH reagent and 10 mL of isooctane. The impingers are connected in series to the sampling system and sample flow is started. The following parameters are recorded on the data sheet (see Figure 3 for an example): date, sampling location, time, ambient temperature, barometric pressure (if available), relative humidity (if available), dry gas meter reading (if appropriate), flow rate, rotometer setting, DNPH reagent batch number, and dry gas meter and pump identification numbers.

10.5 The sampler is allowed to operate for the desired period, with periodic recording of the variables listed above. The total flow should not exceed ∿80 liters. The operator must ensure that at least 2-3 mL of isooctane remains in the first impinger at the end of the sampling interval (i.e. for high ambient temperatures lower sampling volumes may be required).

10.6 At the end of the sampling period the parameters listed in 10.4 are recorded and the sample flow is stopped. If a dry gas meter is not used the flow rate must be checked at the end of the sampling interval. If the flow rate at the beginning and end of the sampling period differ by more than 15% the sample should be marked as suspect.

10.7 Immediately after sampling the impingers are removed from the sampling system. The contents of the first impinger are emptied into a clean 50 mL glass vial having a teflon-lined screw cap. The first impinger is then rinsed with the contents of the second (backup) impinger and the rinse solution is added to the vial. The vial is then capped, sealed with teflon tape and placed in a friction top can containing 1-2 inches of granular charcoal. The samples are stored in the can, refrigerated until analysis.

10.8 If a dry gas meter or equivalent total flow indicator is not used the average sample flow rate must be calculated according to the following equation:

$$Q_A = \frac{Q_1 + Q_2 \ldots\ldots Q_N}{N}$$

where

Q_A = Average flow rate in mL/minute.

$Q_1, Q_2, \ldots Q_N$ = Flow rates determined at the beginning, end, and intermediate points during sampling.

N = Number of points averaged.

10.9 The total flow is then calculated using the following equation:

$$V_m = \frac{(T_2 - T_1)Q_A}{1000}$$

V_m = Total volume sampled in liters at measured temperature and pressure

T_2 = Stop time

T_1 = Start time (T_2-T_1 given in minutes)

11. Sample Analysis

11.1 Sample Preparation

11.1.1 The samples are returned to the laboratory in 50 mL screw-capped glass vials. To recover the DNPH derivatives the following procedure is employed.

11.1.2 The vials are shaken in a horizontal position on a reciprocating shaker for 10 minutes. The vials are then removed from the shaker and the isooctane layer is removed and placed in a second clean 50 mL screw-capped glass vial using a disposable pipette.

11.1.3 The remaining aqueous layer is extracted with 10 mL of 70/30 (V/V) hexane/methylene chloride in the same manner as described in 11.1.2. The organic layer is removed and combined with the isooctane extract.

11.1.4 The combined organic extracts are then concentrated to dryness at 40°C under a steam of pure nitrogen. When the sample just reaches dryness the vial is removed from the nitrogen stream and a measured volume (2-5 mL) of methanol is added to the vial. The vial is tightly capped and stored refrigerated until analysis.

11.2 HPLC Analysis

11.2.1 The instrument is assembled and calibrated as described in Section 12. Prior to each analysis the detector baseline is checked to ensure stable operation.

11.2.2 A 5-25 µL aliquot of the sample, dissolved in methanol,is drawn into a clean HPLC injection syringe. The sample injection loop is loaded and an injection is made. The data system, if available, is activated simultaneously with the injection and the point of injection is marked on the stripchart recorder.

11.2.3 After approximately one minute, the injection valve is returned to "load" position and the syringe and valve are flushed with methanol in preparation for the next sample analysis.

11.2.4 After elution of the last component of interest the acquisition is terminated and the component concentrations are calculated as described in Section 13.

11.2.5 After a stable baseline is achieved the system can be used for further sample analyses as described above.

11.2.6 If the concentration of a component exceeds the linear range of the instrument the sample should be diluted with methanol, or a smaller volume can be injected onto the HPLC.

12. HPLC Assembly and Calibration

12.1 The HPLC system is assembled as shown in Figure 3. The typical chromatographic performance and operating parameters are shown in Figure 4.

12.2 Mobile phase is prepared by mixing 800 mL of methanol and 200 mL of reagent water. This mixture is filtered through a 0.22 μm polyester membrane filter in an all glass and teflon suction filtration apparatus. The filtered mobile phase is degassed by purging with helium gas for 10-15 minutes (∿ 100 mL/minute) or by heating to ∿60°C for 5-10 minutes in an Erlenmeyer flask covered with a watch glass. A constant back pressure restrictor (∿ 50 psi) or short length (6-12 inches) of 0.01 inch I.D. teflon tubing should be placed after the detector to further eliminate mobile phase outgassing.

12.3 The mobile phase is placed in the HPLC solvent reservoir and the pump flow is set at 1 mL/minute and allowed to pump for 20-30 minutes prior to the first analysis. The detector is switched on at least 30 minutes prior to the first analysis and the detector output is displayed on a stripchart recorder or similar output device at a sensitivity of .008

absorbance units full scale (AUFS). Once a stable baseline is achieved the system is ready for calibration.

12.4 Calibration standards are prepared in methanol from the solid DNPH derivatives. Individual stock solutions of ∿ 100 mg/L are prepared by dissolving 10 mg of the solid derivative in 100 mL of methanol. These individual solutions are used to prepare calibration standards containing all of the derivatives of interest at concentrations of 0.1 - 10 mg/L, which spans the concentration of interest for most ambient air work.

12.5 All calibration runs are performed as described for sample analyses in Section 11. Before initial use the operator should inject a series of calibration standards (at least three levels) spanning the concentration range of interest. Using the UV detector, a linear response range of approximately 0.1 to 10 mg/L should be achieved, for ∿ 10 μL injection volumes. Linear response is indicated where a correlation coefficient of a least 0.999 for a linear least squares fit of the data (concentration versus area response) is obtained.

12.6 Once linear response has been documented an intermediate concentration standard near the anticipated levels for each component, but at least 10 times the detection limit, should be chosen for daily calibration. The response for the various DNPH components should be within 10% day to day. If greater variability is observed more frequent calibration may be required to ensure that valid results are obtained.

12.7 The response for each component in the daily calibration standard is used to calculate a response factor according to the following equation:

$$RF_c = \frac{C_c \times V_I}{R_c}$$

where

RF_c = response factor for the component of interest in nanograms injected/response unit (usually area counts).

C_c = concentration of component in the daily calibration standard (mg/L).

V_I = volume of calibration standard injected (µL).

R_c = response for component of interest in calibration standard (area counts).

13. Calculations

13.1 The volume of air sampled is often reported uncorrected for atmospheric conditions (i.e. under ambient conditions). However, the value can be adjusted to standard conditions (25°C and 760 mm pressure) using the following equation:

$$V_s = V_m \times \frac{P_A}{760} \times \frac{298}{273 + T_A}$$

where

V_s = total sample volume at 25°C and 760 mm Hg pressure (liters).

V_m = total sample volume under ambient conditions (liters). Calculated in 10.9 or from dry gas meter reading.

P_A = ambient pressure (mmHg).

T_A = ambient temperature (°C).

13.2 The concentration of each aldehyde (as the DNPH derivative is calculated for each sample using the following equation:

$$W_d = RF_c \times R_d \times \frac{V_E}{V_I}$$

where

W_d = total quantity of derivative in the sample (µg).

RF_c = response factor calculated in 12.7

R_d = response for component in sample extract (area counts or other response units).

V_E = final volume of sample extract (mL).

V_I = volume of extract injected onto the HPLC system (µL).

13.3 The concentration of aldehyde in the original sample is calculated from the following equation:

$$C_A = \frac{W_d}{V_m (\text{or } V_s\ )} \times \frac{MW_A}{MW_d} \times 1000$$

where

C_A = concentration of aldehyde in the original sample (ng/L).

V_m or V_s are as specified in Section 13.1.

MW_A and MW_d are the molecular weights (g/mole) of the aldehyde and its corresponding DNPH derivative, respectively.

13.4 The aldehyde concentrations can be converted to ppbv using the following equation:

$$C_A(\text{ppbv}) = C_A(\text{ng/L}) \times \frac{24.4}{MW_A}$$

where

C_A(ng/L) is calculated using V_s.

14. Performance Criteria and Quality Assurance

This section summarizes the quality assurance (QA) measures and provides guidance concerning performance criteria which should be achieved within each laboratory.

14.1 Standard Operating Procedures (SOPs).

14.1.1 Each user should generate SOPs describing the following activities as accomplished in their laboratory: 1) assembly, calibration and operation of the sampling system, 2) preparation, purification, storage and handling of DNPH reagent and samples, 3) assembly, calibration and operation of the HPLC system, and 4) all aspects of data recording and processing.

14.1.2 SOPs should provide specific stepwise instructions and should be readily available to, and understood by, the laboratory personnel conducting the work.

14.2 HPLC System Performance

14.2.1 The general appearance of the HPLC chromatograph should be similar to that shown in Figure 4.

14.2.2 The HPLC system efficiency and peak asymmetry factor should be determined in the following manner. A solution of the formaldehyde DNPH derivative corresponding to at least 20 times the detection limit should be injected with the recorder chart sensitivity and speed set to yield a peak approximately 75% of full scale and 1 cm wide at half height. The peak asymmetry factor is determined as shown in Figure 5, and should be between 0.8 and 1.8.

14.2.3 HPLC system efficiency is calculated according to the following equation:

$$N = 5.54 \left(\frac{t_r}{W_{1/2}}\right)$$

where

N = column efficiency, theoretical plates
t_r = retention time of components (seconds)
$W_{1/2}$ = width of component peak at half height (seconds)

A column efficiency of >5,000 should be obtained.

14.2.4 Precision of response for replicate HPLC injections should be ± 10% or less, day to day, for calibration standards. Precision of retention times should be ± 2%, on a given day.

14.3 Process Blanks

14.3.1 Prior to use a 10 mL aliquot of each batch of DNPH reagent should be analyzed as described in Section 11. In general, formaldehyde levels equivalent to >5 ng/L in a 60 liter sample should be achieved and other aldehyde levels should be <1 ng/L.

14.3.2 At least one field blank should be shipped and analyzed with each group of samples. The field blank is treated identically to the samples except that no air is drawn through the reagent. The same performance criteria described in 14.3.1 should be met for process blanks.

14.4 Method Precision and Accuracy

14.4.1 Analysis of replicate samples indicates a precision of ± 15-20% relative standard deviation can be readily achieved. Each laboratory should collect parallel samples periodically (at least one for each batch of samples) to document their precision in conducting the method.

14.4.2 Precision for replicate HPLC injections should be ± 10% or better, day to day, for calibration standards.

14.4.3 Method accuracy is difficult to assess because of the difficulty in generating accurate gaseous standards. Literature results indicate (1-3) recoveries of 75% or greater are achieved for a broad range of aldehydes. Each laboratory should periodically collect field samples wherein the impinger solution is spiked with a known quantity of the compound of interest, prepared as a dilute methanol solution. Formaldehyde cannot be spiked in this manner and therefore a solution of the DNPH derivative should be used for spiking purposes.

14.4.4 Before initial use of the method each laboratory should generate triplicate spiked samples at a minimum of three concentration levels, bracketing the range of interest for each compound. Triplicate nonspiked samples must also be processed. Recoveries of >70 ± 20% and blank levels of <5 ng/L for formaldehyde and 1 ng/L for the other compounds (assuming a 60 liter air sample) should be achieved.

References

(1) Grosjean, D., Fung, K., and Atkinson, R., "Measurements of Aldehydes in the Air Environment", Proc. Air Poll. Cont. Assoc., Paper 80-50.4, 1980.

(2) Grosjean, D. and Fung K., "Collection Efficiencies of Cartridges and Micro-Impingers for Sampling of Aldehydes in Air as 2,4-Dinitrophenylhydrazones", Anal. Chem. 54, 1221-1224, 1982.

(3) Grosjean, D., "Formaldehyde and Other Carbonyls in Los Angeles Ambient Air", Environ. Sci. Technol. 16, 254-262, 1982.

(4) Riggin, R. M., "Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air", EPA-600/4-83-027. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1983.

(5) Annual Book of ASTM Standards, Part 11.03, "Atmospheric Analysis", American Society for Testing and Material, Philadelphia, Pennsylvania, 1983.

(6) Berry, D. A., Holdren, M. W., Lyon, T. F., Riggin, R. M., and Spicer, C. W., "Turbine Engine Exhaust Hydrocarbon Analysis-Interim Report on Task 1 and 2", Report on Contract No. F-08635-82-C-0131, Air Force Engineering and Services Center, Tyndall AFB, Florida, 1983.

(7) Shiner, R., Fuson, R., and Curtin, D., "The Systematic Identification of Organic Compounds", John Wiley and Sons, Inc., 5th ed., New York, 1964.

(8) "Method 6 Determination of SO_2 Emissions from Stationary Sources", Federal Register, Vol. 42., No. 160, August 1977.

TABLE 1. ALDEHYDES AND KETONES FOR WHICH THE METHOD HAS BEEN EVALUATED

	Molecular Weight		Typical Relative Retention Time(a)
Compound	Derivative	Compound	
Formaldehyde	210	30	1.0
Acetaldehyde	224	44	1.3
Acrolein	236	56	1.6
Propanal	238	58	1.7
Acetone	238	58	1.9(b)
Crotonaldehyde	250	70	2.3
Isobutyraldehyde	252	72	2.4
Methyl Ethyl Ketone	252	72	2.8
Benzaldehyde	286	106	3.2
Pentanal	266	86	3.7
o-Tolualdehyde	300	120	4.8
m-Tolualdehyde	300	120	5.1
p-Tolualdehyde	300	120	5.3
Hexanal	280	100	5.7

(a) Using HPLC conditions shown in Figure 4.
Formaldehyde = 1.0

(b) Acetone background levels in the reagent prevent its determination in most cases.

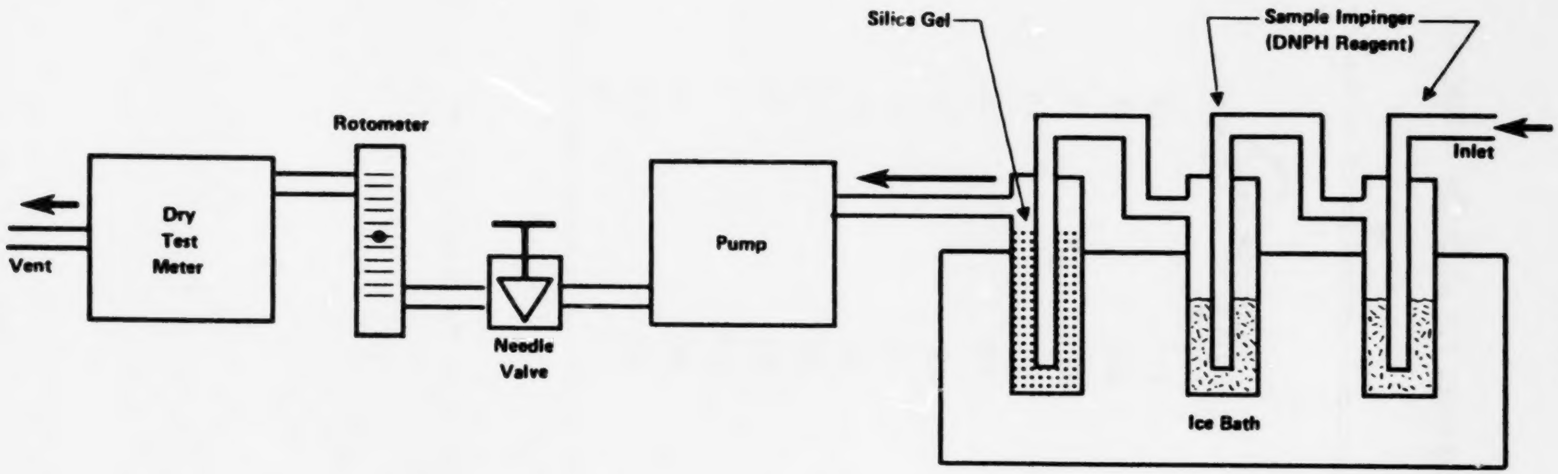

Silica Gel
Sample Impinger
(DNPH Reagent)
Inlet
Rotometer
Dry
Test
Meter
Vent
Needle
Valve
Pump
Ice Bath

FIGURE 1. TYPICAL SAMPLING SYSTEM

SAMPLING DATA SHEET
(One Sample Per Data Sheet)

PROJECT: ____________________

SITE: ____________________

LOCATION: ____________________

INSTRUMENT MODEL NO: ____________

PUMP SERIAL NO: ____________

DATE(S) SAMPLED: ____________________

TIME PERIOD SAMPLED: ________________

OPERATOR: ____________________

CALIBRATED BY: ____________________

SAMPLING DATA

Sample Number: ____________________

Start Time: ________ Stop Time: ________

Time	Dry Gas Meter Reading	Rotameter Reading	Flow Rate,*Q ml/Min	Ambient Temperature °C	Barometric Pressure, mmHg	Relative Humidity, %	Comments
1.							
2.							
3.							
4.							
N.							

Total Volume Data**

V_m = (Final - Initial) Dry Gas Meter Reading, or = ______ Liters

$$= \frac{Q_1 + Q_2 + Q_3 \ldots Q_N}{N} \times \frac{1}{1000 \times (\text{Sampling Time in Minutes})}$$ = ______ Liters

* Flowrate from rotameter or soap bubble calibrator (specify which).

** Use data from dry gas meter if available.

FIGURE 2. EXAMPLE SAMPLING DATA SHEET

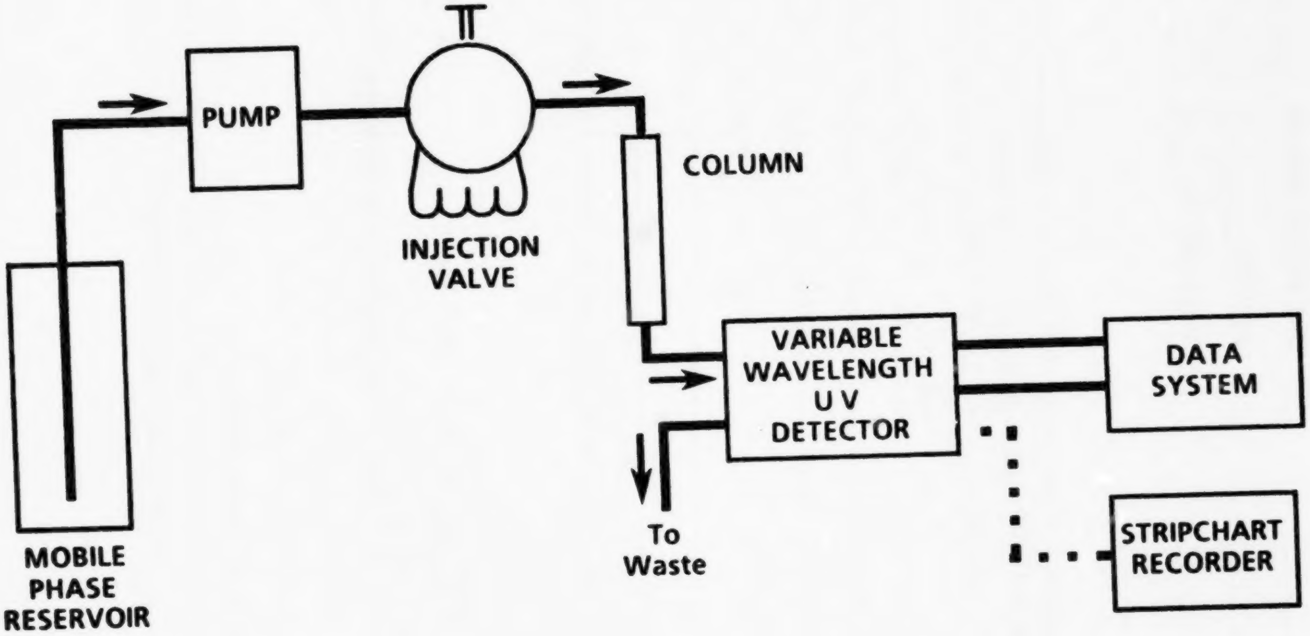

PUMP
INJECTION VALVE
COLUMN
VARIABLE WAVELENGTH U V DETECTOR
DATA SYSTEM
STRIPCHART RECORDER
To Waste
MOBILE PHASE RESERVOIR

FIGURE 3. TYPICAL HPLC SYSTEM

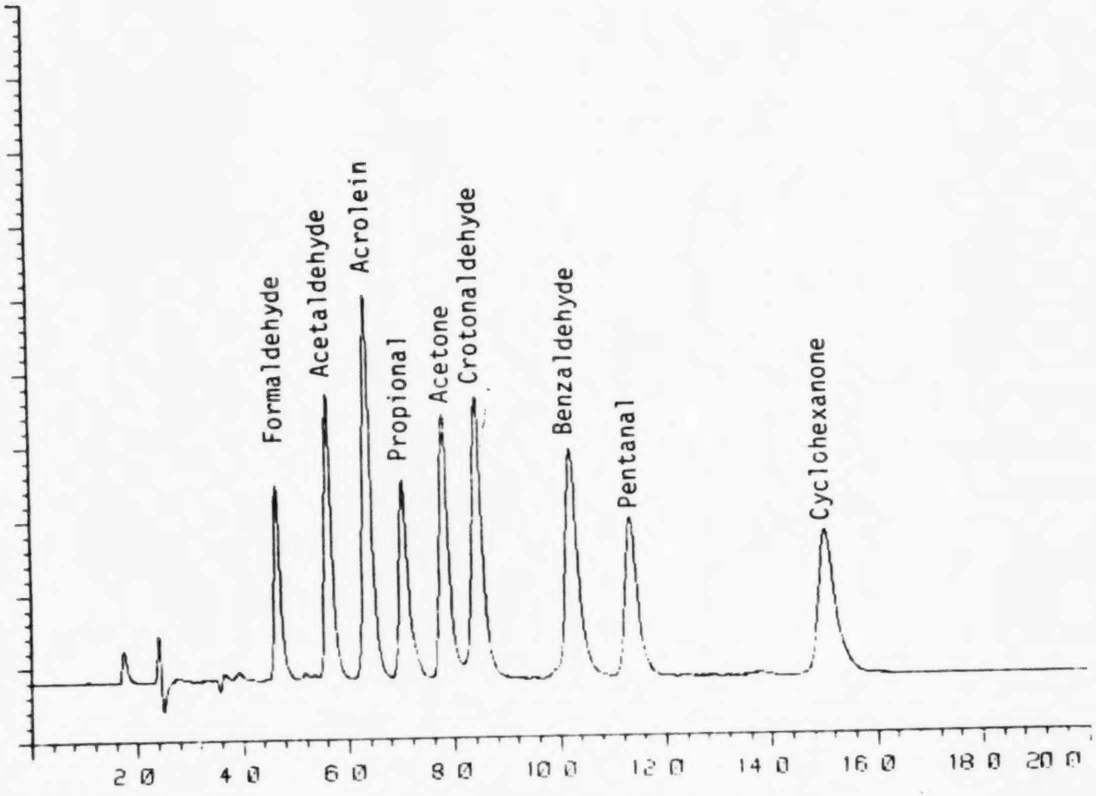
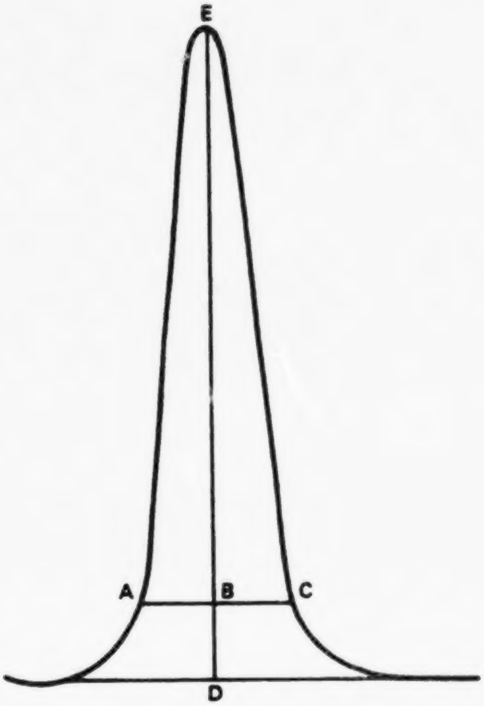


FIGURE 4. TYPICAL HPLC CHROMATOGRAM

Column - Zorbax ODS, 250 x 4.6 mm
Mobile Phase - 80/20 Methanol/H_2O
Flow Rate - 1 mL/Minute
Detector - UV at 370 nm



$$\text{Asymmetry Factor} = \frac{BC}{AB}$$

Example Calculation:

Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm

Therefore: $\text{Asymmetry Factor} = \frac{12}{11} = 1.1$

FIGURE 5. PEAK ASYMMETRY CALCULATION

APPENDIX A—EPA METHOD 608

United States
Environmental Protection
Agency

Environmental Monitoring and
Support Laboratory
Cincinnati OH 45268

Research and Development

Test Method

Organochlorine Pesticides and PCBs — Method 608

1. Scope and Application

1.1 This method covers the determination of certain organochlorine pesticides and PCBs. The following parameters can be determined by this method:

Parameter	STORET No.	CAS No.
Aldrin	39330	309-00-2
α-BHC	39337	319-84-6
β-BHC	39338	319-85-7
δ-BHC	34259	319-86-8
γ-BHC	39340	58-89-9
Chlordane	39350	57-74-9
4,4′-DDD	39310	72-54-8
4,4′-DDE	39320	72-55-9
4,4′-DDT	39300	50-29-3
Dieldrin	39380	60-57-1
Endosulfan I	34361	959-98-8
Endosulfan II	34356	33212-65-9
Endosulfan sulfate	34351	1031-07-8
Endrin	39390	72-20-8
Endrin aldehyde	34366	7421-93-4
Heptachlor	39410	76-44-8
Heptachlor epoxide	39420	1024-57-3
Toxaphene	39400	8001-35-2
PCB-1016	34671	12674-11-2
PCB-1221	39488	11104-28-2
PCB-1232	39492	11141-16-5
PCB-1242	39496	53469-21-9
PCB-1248	39500	12672-29-6
PCB-1254	39504	11097-69-1
PCB-1260	39508	11096-82-5

1.2 This is a gas chromatographic (GC) method applicable to the determination of the compounds listed above in municipal and industrial discharges as provided under 40 CFR 136.1. When this method is used to analyze unfamiliar samples for any or all of the compounds above, compound identifications should be supported by at least one additional qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm measurements made with the primary column. Method 625 provides gas chromatograph/mass spectrometer (GC/MS) conditions appropriate for the qualitative and quantitative confirmation of results for all of the parameters listed above, using the extract produced by this method.

1.3 The method detection limit (MDL, defined in Section 14.1)[1] for each parameter is listed in Table 1. The MDL for a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix.

1.4 The sample extraction and concentration steps in this method are essentially the same as in methods 606, 609, 611 and 612. Thus, a single sample may be extracted to measure the parameters included in the scope of each of these methods. When cleanup is required, the concentration levels must be high enough to permit selection of aliquots as necessary to apply appropriate cleanup procedures. The analyst is allowed the latitude to select gas chromatographic conditions appropriate for the simultaneous measurement of combinations of these parameters.

1.5 Any modification of this method, beyond those expressly permitted, shall be considered as major modifications subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatography and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

2. Summary of Method

2.1 A measured volume of sample, approximately one-liter, is solvent extracted with methylene chloride using a separatory funnel. The methylene chloride extract is dried and exchanged to hexane, during concentration to a final volume of 10 mL or less. Gas chromatographic conditions are described which permit the separation and measurement of the parameters in the extract by electron capture GC[2].

2.2 The method provides a Florisil column procedure and elemental sulfur removal procedure to aid in the elimination of interferences that may be encountered.

3. Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.5.

3.1.1 Glassware must be scrupulously cleaned[3]. Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. This should be followed by detergent washing with hot water, and rinses with tap water and distilled water. It should then be drained dry and heated in a muffle furnace at 400 °C for 15 to 30 minutes. Some thermally stable materials, such as PCBs, may not be eliminated by this treatment. Solvent rinses with acetone and pesticide quality hexane may be substituted for the muffle furnace heating. Thorough rinsing with such solvents usually elminates PCB interference. Volumetric ware should not be heated in a muffle furnace. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences by phthalate esters can pose a major problem in pesticide analysis when using the elution capture detector. These compounds generally appear in the chromatogram as large eluting peaks, especially in the 15 and 50% fractions from Florisil. Common flexible plastics contain varying amounts of phthalates. These phthalates are easily extracted or leached from such materials during laboratory operations. Cross contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent wetted surfaces are handled. Interferences from phthalates can best be minimized by avoiding the use of plastics in the laboratory. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination[4,5]. The interferences from phthalate esters can be avoided by using a microcoulometric or electrolytic conductivity detector.

3.3 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled. The cleanup procedures in Section 11 can be used to overcome many of these interferences, but unique samples may require additional cleanup approaches to achieve the MDL listed in Table 1.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified[6-8] for the information of the analyst.

4.2 The following parameters covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: 4,4'-DDT, 4,4'-DDD, the BHCs, and the PCBs. Primary standards of these toxic compounds should be prepared in a hood.

5. Apparatus and Materials

5.1 Sampling equipment, for discrete or composite sampling.

5.1.1 Grab sample bottle—Amber glass, one-liter or one-quart volume, fitted with screw caps lined with Teflon. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The container must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

5.1.2 Automatic sampler (optional)—Must incorporate glass sample containers for the collection of a minimum of 250 mL. Sample containers must be kept refrigerated at 4 °C and protected from light during compositing. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used. Before use, however, the compressible tubing should be thoroughly rinsed with methanol, followed by repeated rinsings with distilled water to minimize the potential for contamination of the sample. An integrating flow meter is required to collect flow proportional composites.

5.2 Glassware (All specifications are suggested. Catalog numbers are included for illustration only).

5.2.1 Separatory funnel—2000-mL, with Teflon stopcock.

5.2.2 Drying column—Chromatographic column approximately 400 mm long × 19 mm ID, with coarse frit.

5.2.3 Chromatographic column—Pyrex, 400 mm long × 22 mm ID, with coarse fritted plate and Teflon stopcock (Kontes K-42054 or equivalent).

5.2.4 Concentrator tube, Kuderna-Danish—10-mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

5.2.5 Evaporative flask, Kuderna-Danish—500-mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

5.2.6 Snyder column, Kuderna-Danish—three-ball macro (Kontes K-503000-0121 or equivalent).

5.2.7 Vials—Amber glass, 10- to 15-mL capacity, with Teflon-lined screw cap.

5.3 Boiling chips—approximately 10/40 mesh. Heat to 400 °C for 30 minutes or Soxhlet extract with methylene chloride.

5.4 Water bath—Heated, with concentric ring cover, capable of temperature control (± 2 °C). The bath should be used in a hood.

5.5 Balance—Analytical, capable of accurately weighing 0.0001 g.

5.6 Gas chromatograph—An analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, gases, detector, and strip-chart recorder. A data system is recommended for measuring peak areas.

5.6.1 Column 1—1.8 m long × 4 mm ID glass, packed with 1.5% SP-2250/1.95% SP-2401 on Supelcoport (100/120 mesh) or equivalent. Column 1 was used to develop the method performance statements in Section 14. Guidelines for the use of alternate column packings are provided in Section 12.1.

5.6.2 Column 2—1.8 m long × 4 mm ID glass, packed with 3% OV-1 on Supelcoport (100/120 mesh) or equivalent.

5.6.3 Detector—Electron capture. This detector has proven effective in the analysis of wastewaters for the parameters listed in the scope, and was used to develop the method performance statements in Section 14. Guidelines for the use of alternate detectors are provided in Section 12.1.

6. Reagents

6.1 Reagent water—Reagent water is defined as a water in which an interferent is not observed at the MDL of each parameter of interest.

6.2 Sodium hydroxide solution (10 N)—(ACS). Dissolve 40g NaOH in reagent water and dilute to 100 mL.

6.3 Sodium thiosulfate—(ACS) Granular.

6.4 Sulfuric acid solution (1 + 1)—(ACS). Slowly, add 50 mL H_2SO_4 (sp. gr. 1.84) to 50 mL of reagent water.

6.5 Acetone, hexane, isooctane (2,2,4-trimethylpentane), methylene chloride—Pesticide quality or equivalent.

6.6 Ethyl ether—Pesticide quality or equivalent, redistilled in glass if necessary.

6.6.1 Must be free of peroxides as indicated by EM Laboratories Quant test strips (Available from Scientific Products Co., Cat. No. P1126-8, and others suppliers.)

6.6.2 Procedures recommended for removal of peroxides are provided with the test strips. After cleanup, 20 mL ethyl alcohol preservative must be added to each liter of ether.

6.7 Sodium sulfate—(ACS) Granular, anhydrous. Purify by heating at 400 °C for 4 hours in a shallow tray.

6.8 Florisil—PR grade (60/100 mesh); purchase activated at 1250 °F and store in dark in glass containers with glass stoppers or foil-lined screw caps. Before use, activate each batch at least 16 hours at 130 °C in a foil covered glass container.

6.9 Mercury—Triple distilled.

6.10 Copper powder—Activated.

6.11 Stock standard solutions (1.00 µg/µL)—Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions.

6.11.1 Prepare stock standard solutions by accurately weighing about 0.0100 grams of pure material. Dissolve the material in isooctane, dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

6.11.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4 °C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Quality control check standards that can be used to determine the accuracy of calibration standards will be available from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

6.11.3 Stock standard solutions must be replaced after six months, or sooner if comparison with check standards indicate a problem.

7. Calibration

7.1 Establish gas chromatographic operating parameters which produce retention times equivalent to those indicated in Table 1. The gas chromatographic system may be calibrated using the external standard technique (Section 7.2) or the internal standard technique (Section 7.3).

7.2 External standard calibration procedure:

7.2.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with isooctane. One of the external standards should be at a concentration near, but above, the MDL and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.2.2 Using injections of 2 to 5 µL of each calibration standard, tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to amount injected (calibration factor) is a constant over the working range (<10% relative standard deviation, RSD), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

7.2.3 The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ± 10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor must be prepared for that compound.

7.3 Internal standard calibration procedure. To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

7.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with isooctane. One of the standards should be at a concentration near, but above, the MDL and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.3.2 Using injections of 2 to 5 µL of each calibration standard, tabulate peak height or area responses against concentration for each compound and internal standard, and calculate response factors (RF) for each compound using equation 1.

Eq. 1. $RF = (A_sC_{is})/(A_{is}C_s)$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

C_{is} = Concentration of the internal standard, (µg/L).

C_s = Concentration of the parameter to be measured, (µg/L).

If the RF value over the working range is a constant (<10% RSD), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is}, vs. RF.

7.3.3 The working calibration curve or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ± 10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that compound.

7.4 The cleanup procedure in Section 11 utilizes Florisil chromatography. Florisil from different batches or sources may vary in absorptive capacity. To standardize the amount of Florisil which is used, the use of lauric acid value(9) is suggested. The referenced procedure determines the adsorption from hexane solution of lauric acid (mg) per gram Florisil. The amount of Florisil to be used for each column is calculated by dividing this factor into 110 and multiplying by 20 g.

7.5 Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of data that is generated. Ongoing performance checks must be compared with established performance criteria to determine if the results of analyses are within accuracy and precision limits expected of the method.

8.1.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 In recognition of the rapid advances that are occurring in chromatography, the analyst is permitted certain options to improve the separations or lower the cost of measurements. Each time such modifications are made to the method, the analyst is required to repeat the procedure in Section 8.2.

8.1.3 The laboratory must spike and analyze a minimum of 10% of all samples to monitor continuing laboratory performance. This procedure is described in Section 8.4.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.2.1 Select a representative spike concentration for each compound to be measured. Using stock standards, prepare a quality control check sample concentrate in acetone 1000 times more concentrated than the selected concentrations. Quality control check sample concentrates, appropriate for use with this method, will be available from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

8.2.2 Using a pipet, add 1.00 mL of the check sample concentrate to each of a minimum of four 1000-mL aliquots of reagent water. A representative wastewater may be used in place of the reagent water, but one or more additional aliquots must be analyzed to determine background levels, and the spike level must exceed twice the background level for the test to be valid. Analyze the aliquots according to the method beginning in Section 10.

8.2.3 Calculate the average percent recovery, (R), and the standard deviation of the percent recovery (s), for the results. Wastewater background corrections must be made before R and s calculations are performed.

8.2.4 Using Table 2, note the average recovery (X) and standard deviation (p) expected for each method parameter. Compare these to the calculated values for R and s. If $s > 2p$ or $|X - R| > 2p$, review potential problem areas and repeat the test.

8.2.5 The U.S. Environmental Protection Agency plans to establish performance criteria for R and s based upon the results of interlaboratory testing. When they become available, these criteria must be met before any samples may be analyzed.

8.3 The analyst must calculate method performance criteria and define the performance of the laboratory for each spike concentration and parameter being measured.

8.3.1 Calculate upper and lower control limits for method performance:

Upper Control Limit (UCL) = R + 3s
Lower Control Limit (LCL) = R − 3s

where R and s are calculated as in Section 8.2.3. The UCL and LCL can be used to construct control charts(10) that are useful in observing trends in performance. The control limits above be replaced by method performance criteria as they become available from the U.S. Environmental Protection Agency.

8.3.2 The laboratory must develop and maintain separate accuracy statements of laboratory performance for wastewater samples. An accuracy statement for the method is defined as R ± s. The accuracy statement should be developed by the analysis of four aliquots of wastewater as described in Section 8.2.2, followed by the calculation of R and s. Alternately, the analyst may use four wastewater data points gathered through the requirement for continuing quality control in Section 8.4. The accuracy statements should be updated regularly(10).

8.4. The laboratory is required to collect a portion of their samples in duplicate to monitor spike recoveries. The frequency of spiked sample analysis must be at least 10% of all samples or one sample per month, whichever is greater. One aliquot of the sample must be spiked and analyzed as described in Section 8.2. If the recovery for a particular parameter does not fall within the control limits for method performance, the results reported for that parameter in all samples processed as part of the same set must be qualified as described in Section 13.5. The laboratory should monitor the frequency of data so qualified to ensure that it remains at or below 5%.

8.5 Before processing any samples, the analyst should demonstrate through the analysis of a one-liter aliquot of reagent water, that all glassware and reagent interferences are under control. Each time a set of samples is extracted or there is a change in reagents, a laboratory reagent blank should be processed as a safeguard against laboratory contamination.

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to monitor the precision of the sampling technique. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column, specific element detector, or mass spectrometer must be used. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance evaluation studies.

9. Sample Collection, Preservation, and Handling

9.1 Grab samples must be collected in glass containers. Conventional sampling practices(11) should be followed, except that the bottle must not be prewashed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be as free as possible of Tygon tubing and other potential sources of contamination.

9.2 The samples must be iced or refrigerated at 4 °C from the time of collection until extraction. If the samples will not be extracted within 72 hours of collection, the sample should be adjusted to a pH range of 5.0 to 9.0 with sodium hydroxide or sulfuric acid. Record the volume of acid or base used. If aldrin is to be determined, add sodium thiosulfate when residual chlorine is present. U.S. Environmental Protection Agency methods 330.4 and 330.5 may be used to measure chlorine residual(12). Field test kits are available for this purpose.

9.3 All samples must be extracted within 7 days and completely analyzed within 40 days of extraction(2).

10. Sample Extraction

10.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a two-liter separatory funnel.

10.2 Add 60 mL methylene chloride to the sample bottle, seal, and shake 30 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for two minutes with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 250-mL Erlenmeyer flask.

10.3 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

10.4 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the Kuderna Danish if the requirements of Section 8.2 are met.

10.5 Pour the combined extract through a drying column containing about 10 cm of anhydrous sodium sulfate, and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and column with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

10.6 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL methylene chloride to the top. Place the K-D apparatus on a hot water bath (60 to 65 °C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes.

10.7 Increase the temperature of the hot water bath to about 80 °C. Momentarily remove the Snyder column, add 50 mL of hexane and a new boiling chip and reattach the Snyder column. Prewet the column by adding about 1 mL of hexane to the top. Concentrate the solvent extract as before. The elapsed time of concentration should be 5 to 10 minutes. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool at least 10 minutes.

10.8 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of hexane. A 5-mL syringe is recommended for this operation. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. If the extracts will be stored longer than two days, they should be transferred to Teflon-sealed screw-cap bottles. If the sample extract requires no further cleanup, proceed with gas chromatographic analysis. If the sample requires cleanup proceed to Section 11.

10.9 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11. Cleanup and Separation

11.1 Cleanup procedures may not be necessary for a relatively clean sample matrix. The cleanup procedures recommended in this method have been used for the analysis of various clean waters and industrial effluents. If particular circumstances demand the use of an alternative cleanup procedure, the analyst must determine the elution profile and demonstrate that the recovery of each compound of interest is no less than 85%. The Florisil column allows for a select fractionation of the compounds and will eliminate polar materials. Elemental sulfur interferes with the electron capture gas chromatography of certain pesticides, but can be removed by the techniques described below.

11.2 Florisil column cleanup:

11.2.1 Add a weight of Florisil (nominally 21 g) predetermined by calibration (Section 7.4 and 7.5), to a chromatographic column. Settle the Florisil by tapping the column. Add sodium sulfate to the top of the Florisil to form a layer 1 to 2 cm deep. Add 60 mL of hexane to wet and rinse the sodium sulfate and Florisil. Just prior to exposure of the sodium sulfate to air, stop the elution of the hexane by closing the stopcock on the chromatography column. Discard the eluate.

11.2.2 Adjust the sample extract volume to 10 mL with hexane and transfer it from the K-D concentrator tube to the Florisil column. Rinse the tube twice with 1 to 2 mL hexane, adding each rinse to the column.

11.2.3 Place a 500-mL K-D flask and clean concentrator tube under the chromatography column. Drain the column into the flask until the sodium sulfate latyer is nearly exposed. Elute the column with 200 mL of 6% ethyl ether in hexane (V/V) (Fraction 1) using a drip rate of about 5 mL/min. Remove the K-D flask and set aside for later concentration. Elute the column again, using 200 mL of 15% ethyl ether in hexane (V/V)(Fraction 2), into a second K-D flask. Perform the third elution using 200 mL of 50% ethyl ether in hexane (V/V)(Fraction 3). The elution patterns for the pesticides an PCB's are shown in Table 2.

11.2.4 Concentrate the eluates by standard K-D techniques (Section 10.6), substituting hexane for the glassware rinses and using the water bath at about 85 °C. Adjust final volume to 10 mL with hexane. Analyze by gas chromatography.

11.3 Elemental sulfur will usually elute entirely in Fraction 1 of the Florisil column cleanup. To remove sulfur interference from this fraction or the original extract, pipet 1.00 mL of the concentrated extract into a clean concentrator tube or Teflon-sealed vial. Add one to three drops of mercury and seal(13). Agitate the contents of the vial for 15 to 30 seconds. Prolonged shaking (two hours) may be required. If so, this may be accomplished with a reciprocal shaker. Alternatively, activated copper powder may be used for sulfur removal(14). Analyze by gas chromatography.

12. Gas Chromatography

12.1 Table 1 summarizes the recommended operating conditions for the gas chromatograph. This table includes retention times and MDL that were obtained under these conditions. Examples of the parameter separations achieved by column 1 are shown in Figures 1 to 10. Other packed columns, chromatographic conditions, or detectors may be used if the requirements of Section 8.2 are met. Capillary (open-tubular) columns may also be used if the relative standard deviations of responses for replicate injections are demonstrated to be less than 6% and the requirements of Section 8.2 are met.

12.2 Calibrate the system daily as described in Section 7.

12.3 If the internal standard approach is being used, the internal standard must be added to the sample extract and mixed thoroughly immediately, before injection into the instrument.

12.4 Inject 2 to 5 μL of the sample extract using the solvent-flush technique(15). Smaller (1.0 μL) volumes can be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 μL, the total extract volume, and the resulting peak size in area or peak height units.

12.5 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time for a compound can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

12.6 If the response for the peak exceeds the working range of the system, dilute the extract and reanalyze.

12.7 If the measurement of the peak response is prevented by the presence of interferences, further cleanup is required.

13. Calculations

13.1 Determine the concentration of individual compounds in the sample.

13.1.1 If the external standard calibration procedure is used, calculate the amount of material injected from the peak response using the calibration curve or calibration factor in Section 7.2.2. The concentration in the sample can be calculated from equation 2:

$$\text{Eq. 2. Concentration, } \mu g/L = \frac{(A)(V_t)}{(V_i)(V_s)}$$

where:

A = Amount of material injected, in nanograms.

V_i = Volume of extract injected (μL).

V_t = Volume of total extract (μL).

V_s = Volume of water extracted (mL).

13.1.2 If the internal standard calibration procedure was used, calculate the concentration in the sample using the response factor (RF) determined in Section 7.3.2 and equation 3.

Eq. 3

$$\text{Concentration, } \mu g/L = \frac{(A_s)(I_s)}{(A_{is})(RF)(V_o)}$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

I_s = Amount of internal standard added to each extract (μg).

V_o = Volume of water extracted, in liters.

13.2 When it is apparent that two or more PCB (Aroclor) mixtures are present, the Webb and McCall procedure(16) may be used to identify and quantify the Aroclors.

13.3 For multicomponent mixtures (chlordane, toxaphene and PCBs) match retention times of peaks in the standards with peaks in the sample. Quantitate every identifiable peak unless interference with individual peaks persist after cleanup. Add peak height or peak area of each identified peak in the chromatogram. Calculate as total response in the sample versus total response in the standard.

13.4 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, report all data obtained with the sample results.

13.5 For samples processed as part of a set where the laboratory spiked sample recovery falls outside of the control limits in Section 8.3, data for the affected parameters must be labeled as suspect.

14. Method Performance

14.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero(1). The MDL concentrations listed in Table 1 were obtained using reagent water(17). Similar results were achieved using representative wastewaters.

14.2 This method has been tested for linearity of spike recovery from reagent water and has been demonstrated to be applicable over the concentration range from 4 × MDL up to 1000 × MDL with the following exceptions: Chlordane recovery at 4 × MDL was low (60%); Toxaphene recovery was demonstrated linear over the range of 10 × MDL to 1000 × MDL(17).

14.3 In a single laboratory (Southwest Research Institute), using spiked wastewater samples, the average recoveries presented in Table 3 were obtained(4). Each spiked sample was analyzed in triplicate on two separate days. The standard deviation of the percent recovery is also included in Table 3.

14.4 The U.S. Environmental Protection Agency is in the process of conducting an interlaboratory method study to fully define the performance of this method.

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Table 1. Chromatographic Conditions and Method Detection Limits

Parameter	Retention Time (min.) Column 1	Column 2	Method Detection Limit µg/L
α-BHC	1.35	1.82	0.003
γ-BHC	.70	2.13	0.004
β-BHC	1.90	1.97	0.006
Heptachlor	2.00	3.35	0.003
δ-BHC	2.15	2.20	0.009
Aldrin	2.40	4.10	0.004
Hepachlor epoxide	3.50	5.00	0.083
Endosulfan I	4.50	6.20	0.014
4,4'-DDE	5.13	7.15	0.004
Dieldrin	5.45	7.23	0.002
Endrin	6.55	8.10	0.006
4,4'-DDD	7.83	9.08	0.011
Endosulfan II	8.00	8.28	0.004
4,4'-DDT	9.40	11.75	0.012
Endrin aldehyde	11.82	9.30	0.023
Endosulfan sulfate	14.22	10.70	0.066
Chlordane	mr	mr	0.014
Toxaphene	mr	mr	0.24
PCB-1016	mr	mr	nd
PCB-1221	mr	mr	nd
PCB-1232	mr	mr	nd
PCB-1242	mr	mr	0.065
PCB-1248	mr	mr	nd
PCB-1254	mr	mr	nd
PCB-1260	mr	mr	nd

Column 1 conditions: Supelcoport (100/120 mesh) coated with 1.5% SP-2250/1.95% SP-2401 packed in a 1.8 m long × 4 mm ID glass column with 5% Methane/95% Argon carrier gas at a flow rate of 60 mL/min. Column temperature isothermal at 200°C, except for PCB-1016 through PCB-1248, which should be measured at 160°C.

Column 2 conditions: Supelcoport (100/120 mesh) coated with 3% OV-1 in a 1.8 m long × 4 mm ID glass column with 5% Methane/95% Argon carrier gas at a flow rate of 60 mL/min. Column temperature, isothermal at 200°C, for the pesticides; 140°C for PCB-1221 and 1232; 170°C for PCB-1016 and 1242 to 1268.

mr — Multiple peak response. See Figures 2 thru 10.

nd — Not determined.

Table 2. Distribution of Chlorinated Pesticides and PCBs into Florisil Column Fractions[2]

Parameter	Percent Recovery by Fraction: Fraction 1	Fraction 2	Fraction 3
Aldrin	100		
α-BHC	100		
β-BHC	97		
δ-BHC	98		
γ-BHC	100		
Chlordane	100		
4,4'-DDD	99		
4,4'-DDE	98		
4,4'-DDT	100		
Dieldrin	0	100	
Endosulfan I	37	64	
Endosulfan	0	7	91
Endosulfan sulfate	0	0	106
Endrin	4	96	
Endrin aldehyde	0	68	26
Heptachlor	100		
Heptachlor epoxide	100		
Toxaphene	96		
PCB-1016	97		
PCB-1221	97		
PCB-1232	95	4	
PCB-1242	97		
PCB-1248	103		
PCB-1254	90		
PCB-1260	95		

Eluant composition by fraction:
Fraction 1 — 6% ethyl ether in hexane
Fraction 2 — 15% ethyl ether in hexane
Fraction 3 — 50% ethyl ether in hexane

Table 3. *Single Operator Accuracy and Precision*

Parameter	*Average Percent Recovery*	*Standard Deviation %*	*Spike Range (μg/L)*	*Number of Analyses*	*Matrix Types*
Aldrin	89	2.5	2.0	15	3
α-BHC	89	2.0	1.0	15	3
β-BHC	88	1.3	2.0	15	3
δ-BHC	86	3.4	2.0	15	3
γ-BHC	97	3.3	1.0	15	3
Chlorane	93	4.1	20	21	4
4-4'-DDD	92	1.9	6.0	15	3
4,4'-DDE	89	2.2	3.0	15	3
4,4'-DDT	92	3.2	8.0	15	3
Dieldrin	95	2.8	3.0	15	2
Endosulfan I	96	2.9	3.0	12	2
Endosulfan II	97	2.4	5.0	14	3
Endosulfan sulfate	99	4.1	15	15	3
Endrin	95	2.1	5.0	12	2
Endrin aldehyde	87	2.1	12	11	2
Heptachlor	88	3.3	1.0	12	2
Heptachlor epoxide	93	1.4	2.0	15	3
Toxaphene	95	3.8	200	18	3
PCB-1016	94	1.8	25	12	2
PCB-1221	96	4.2	55-110	12	2
PCB-1232	88	2.4	110	12	2
PCB-1242	92	2.0	28-56	12	2
PCB-1248	90	1.6	40	12	2
PCB-1254	92	3.3	40	18	3
PCB-1260	91	5.5	80	18	3

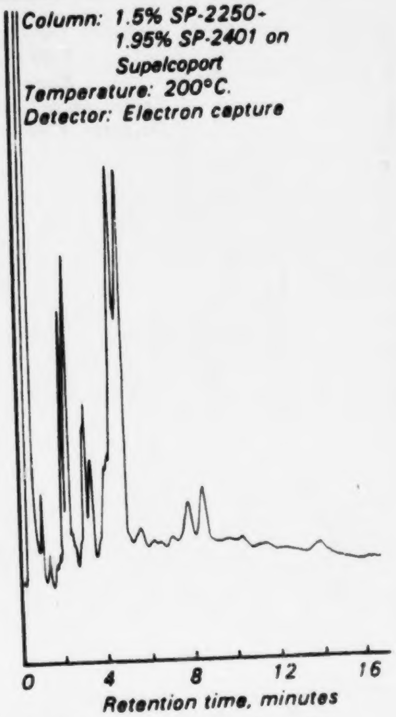

Figure 2. *Gas chromatogram of chlordane.*

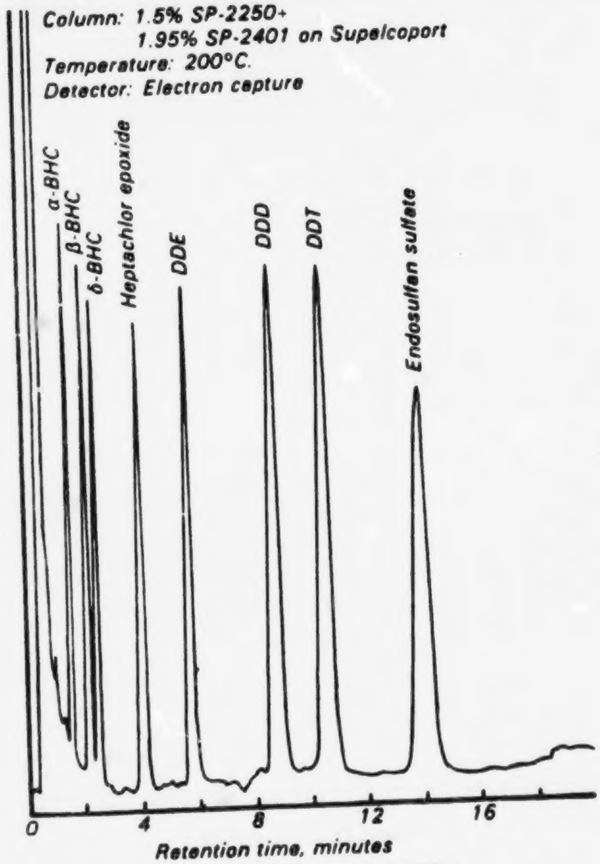

Figure 1. *Gas chromatogram of pesticides.*

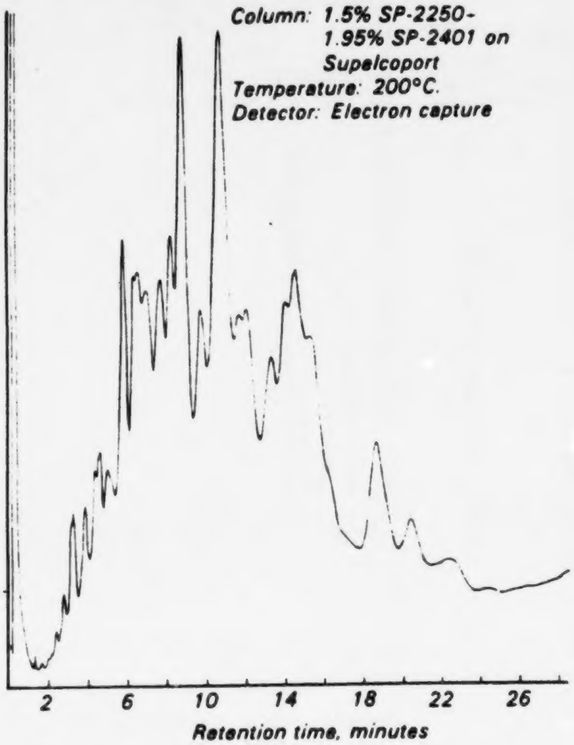

Figure 3. *Gas chromatogram of toxaphene.*

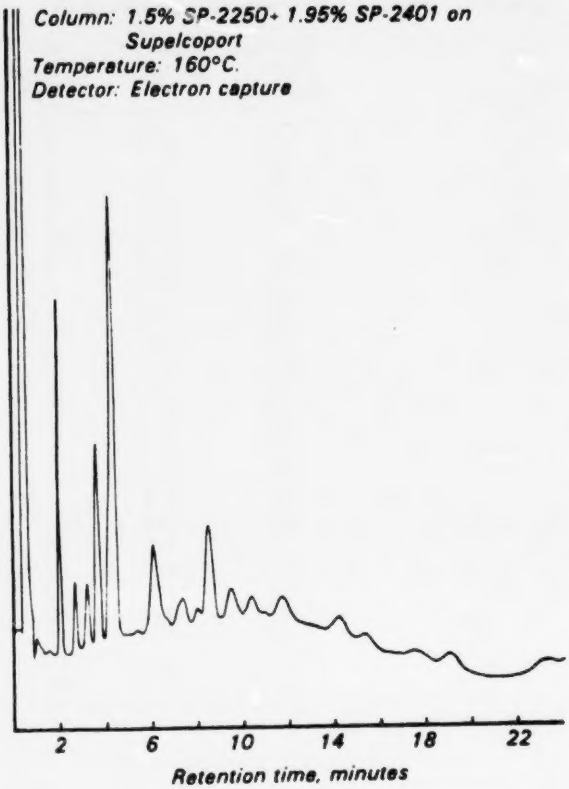

Figure 5. *Gas chromatogram of PCB-1221.*

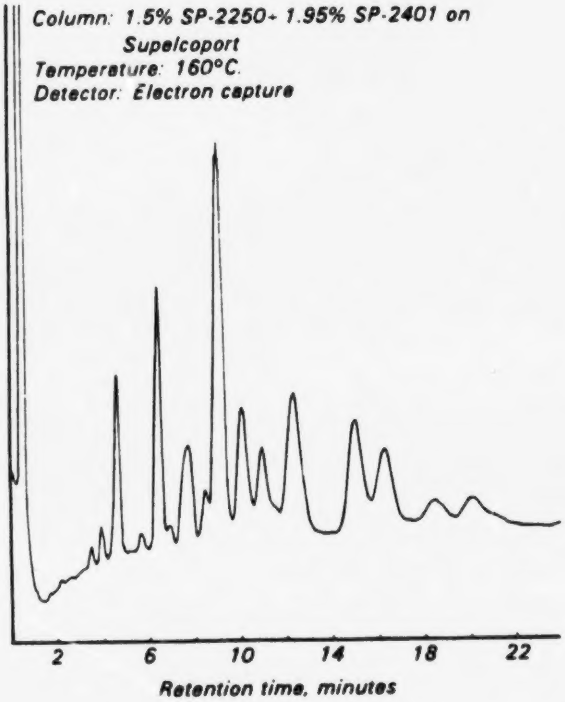

Figure 4. *Gas chromatogram of PCB-1016.*

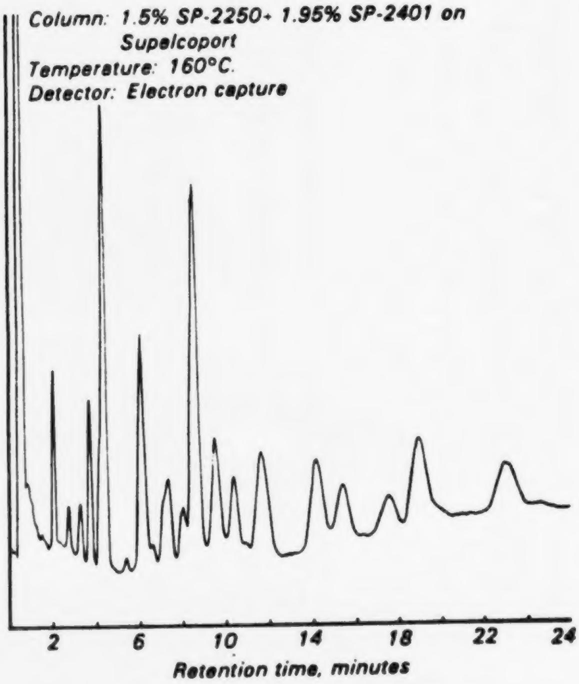

Figure 6. *Gas chromatogram of PCB-1232.*

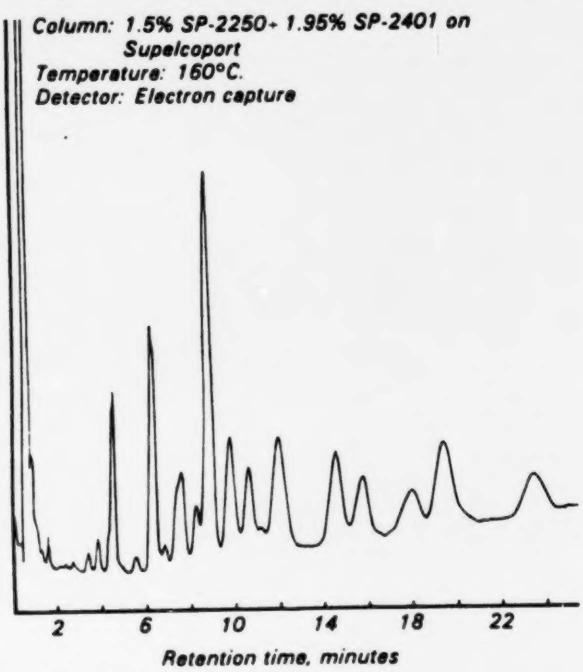
Column: 1.5% SP-2250+ 1.95% SP-2401 on
Supelcoport
Temperature: 160°C.
Detector: Electron capture

Figure 7. Gas chromatogram of PCB-1242.

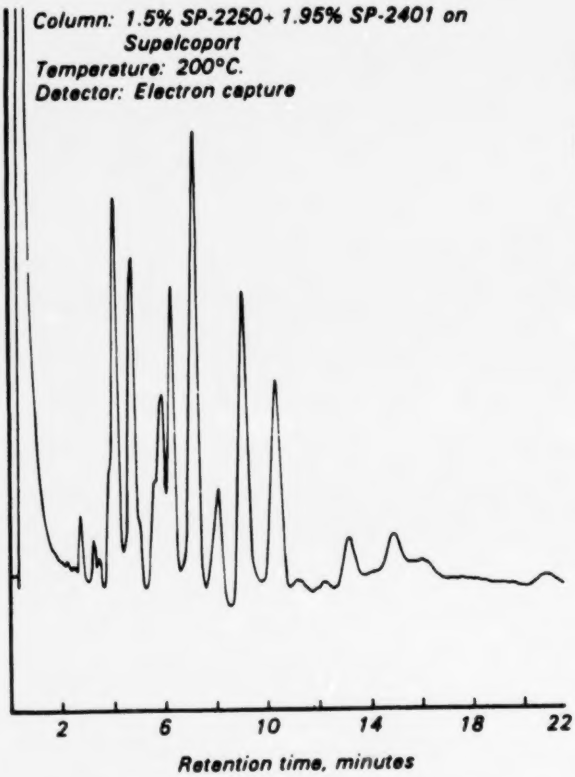
Column: 1.5% SP-2250+ 1.95% SP-2401 on
Supelcoport
Temperature: 200°C.
Detector: Electron capture

Figure 9. Gas chromatogram of PCB-1254.

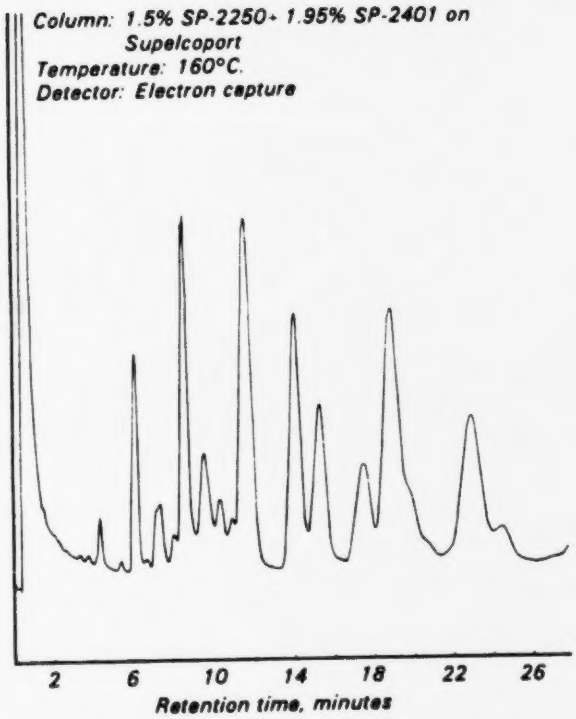
Column: 1.5% SP-2250+ 1.95% SP-2401 on
Supelcoport
Temperature: 160°C.
Detector: Electron capture

Figure 8. Gas chromatogram of PCB-1248.

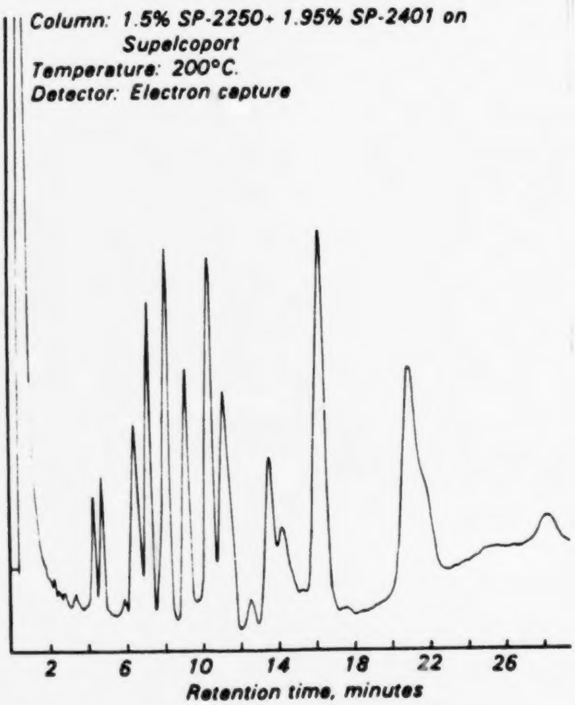
Column: 1.5% SP-2250+ 1.95% SP-2401 on
Supelcoport
Temperature: 200°C.
Detector: Electron capture

Figure 10. Gas chromatogram of PCB-1260.

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METHOD FOR THE DETERMINATION OF PHOSGENE IN AMBIENT AIR USING HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

1. Scope

1.1 This document describes a method for determination of phosgene in ambient air, in which phosgene is collected by passage of the air through a solution of aniline, forming carbanilide. The carbanilide is determined by HPLC. The method can be used to detect phosgene at the 0.1 ppbv level.

1.2 Precision for phosgene spiked into a clean air stream is ±15-20% relative standard deviation. Recovery is quantitative within that precision, down to less than 3 ppbv. This method has been developed and tested by a single laboratory(1), and, consequently, each laboratory desiring to use the method should acquire sufficient precision and recovery data to verify performance under those particular conditions. This method is more sensitive, and probably more selective, than the standard colorimetric procedure currently in widespread use for workplace monitoring(2).

2. Applicable Documents

2.1 ASTM Standards

D1356 - Definitions of Terms Related to Atmospheric Sampling and Analysis(3).

2.2 Other Documents

Standard NIOSH Procedure for Phosgene(2).

U.S. EPA Technical Assistance Document(4).

3. Summary of Method

3.1 Ambient air is drawn through a midget impinger containing 10 mL of 2/98 aniline/toluene (by volume). Phosgene readily reacts with aniline to form carbanilide (1,3-diphenylurea), which is stable indefinitely.

3.2 After sampling, the impinger contents are transferred to a screw-capped vial having a Teflon-lined cap and returned to the laboratory for analysis.

3.3 The solution is taken to dryness by heating to 60°C on an aluminum heating block under a gentle stream of pure nitrogen gas. The residue is dissolved in 1 mL of acetonitrile.

3.4 Carbanilide is determined in the acetonitrile solution using reverse-phase HPLC with an ultraviolet absorbance (UV) detector operating at 254 nm.

4. Significance

4.1 Phosgene is widely used in industrial operations, primarily in the synthetic organic chemicals industry. In addition, phosgene is produced by photochemical degradation of chlorinated hydrocarbons (e.g., trichloroethylene) emitted from various sources. Although phosgene is acutely toxic, its effects at low levels (i.e., 1 ppbv and below) are unknown. Nonetheless, its emission into and/or formation in ambient air is of potential concern.

4.2 The conventional method for phosgene has utilized a colorimetric procedure involving reaction with 4,4'-nitrobenzyl pyridine in diethyl phthalate. This method cannot detect phosgene levels below 10 ppbv and is subject to numerous interferences. The method described herein is more sensitive (0.1 ppbv detection limit) and is believed to be more selective due to the chromatographic separation step. However, the method needs to be more rigorously tested for interferences before its degree of selectivity can be firmly established.

5. Definitions

Definitions used in this document and in any user-prepared SOPs should be consistent with ASTM D1356 (3). All abbreviations and symbols are defined within this document at the point of use.

6. Interferences

6.1 There are very few interferences in the method, although this aspect of the method needs to be more thoroughly investigated. Ambient levels of nitrogen oxides, ozone, water vapor, and SO_2 are known not to interfere. Chloroformates can cause interferences by reacting with the aniline to form urea, which produces a peak that overlies the carbanilide peak in the HPLC trace. Presence of chloroformates should be documented before use of this method. However, the inclusion of a HPLC step overcomes most potential interferences from other organic compounds. High concentrations of acidic materials can cause precipitation of aniline salts in the impinger, thus reducing the amount of available reagent.

6.2 Purity of the aniline reagent is a critical factor, since traces of carbanilide have been found in reagent-grade aniline. This problem can be overcome by vacuum distillation of aniline in an all-glass apparatus.

7. Apparatus

7.1 Isocratic high performance liquid chromatography (HPLC) system consisting of a mobile-phase reservoir, a high-pressure pump, an injection valve, a Zorbax ODS or C-18 reverse-phase column, or equivalent (25 cm x 4.6 mm ID), a variable-wavelength UV detector operating at 254 nm, and a data system or strip-chart recorder (Figure 1).

7.2 Sampling system - capable of accurately and precisely sampling 100-1000 mL/minute of ambient air (Figure 2).

7.3 Stopwatch.

7.4 Friction-top metal can, e.g., one-gallon (paint can) - to hold sampling reagent and samples.

7.5 Thermometer - to record ambient temperature.

7.6 Barometer (optional).

7.7 Analytical balance - 0.1 mg sensitivity.

7.8 Midget impingers - jet inlet type, 25 mL.

7.9 Nitrogen evaporator with heating block - for concentrating samples.

7.10 Suction filtration apparatus - for filtering HPLC mobile phase.

7.11 Volumetric flasks - 100 mL and 500 mL.

7.12 Pipettes - various sizes, 1-10 mL.

7.13 Helium purge line (optional) - for degassing HPLC mobile phase.

7.14 Erlenmeyer flask, 1-L - for preparing HPLC mobile phase.

7.15 Graduated cylinder, 1 L - for preparing HPLC mobile phase.

7.16 Microliter syringe, 10-25 uL - for HPLC injection.

8. Reagents and Materials

8.1 Bottles, 16 oz. glass, with Teflon-lined screw cap - for storing sampling reagent.

8.2 Vials, 20 mL, with Teflon-lined screw cap - for holding samples and extracts.

8.3 Granular charcoal.

8.4 Acetonitrile, toluene, and methanol - distilled in glass or pesticide grade.

8.5 Aniline - 99+%, gold label from Aldrich Chemical Co., or equivalent.

8.6 Carbanilide - highest purity available; Aldrich Chemical Co., or equivalent.

8.7 Nitrogen, compressed gas cylinder - 99.99% purity for sample evaporation.

8.8 Polyester filters, 0.22 um - Nuclepore, or equiv.

9. Preparation of Sampling Reagent

9.1 Sampling reagent is prepared by placing 5.0 mL of aniline in a 250-mL volumetric flask and diluting to the mark with toluene. The flask is inverted 10-20 times to mix the reagent. The reagent is then placed in a clear 16-ounce bottle with a Teflon-lined screw cap. The reagent is refrigerated until use.

9.2 Before use, each batch of reagent is checked for purity by analyzing a 10-mL portion according to the procedure described in Section 11. If acceptable purity (<50 ng of carbanilide per 10 mL of reagent) is not obtained, the aniline or toluene is probably contaminated.

10. Sampling

10.1 The sampling apparatus is assembled and should be similar to that shown in Figure 2. EPA Method 6 uses essentially the same sampling system (5). All glassware (e.g., impingers, sampling bottles, etc.) must be thoroughly rinsed with methanol and oven-dried before use.

10.2 Before sample collection, the entire assembly (including empty sample impingers) is installed and the flow rate checked at a value near the desired rate. Flow rates greater than 1000 mL/minute ($\pm 2\%$) should not be used because impinger collection efficiency may decrease. Generally, calibration is accomplished using a soap bubble flow meter or calibrated wet test meter connected to the flow exit, assuming that the entire system is sealed. ASTM Method D3686 describes an appropriate calibration scheme that does not require a sealed-flow system downstream of the pump (3).

10.3 Ideally, a dry gas meter is included in the system to record total flow, if the flow rate is sufficient for its use. If a dry gas meter is not available, the operator must measure and record the sampling flow rate at the beginning and end of the sampling period to determine sample volume. If the sampling time exceeds two hours, the flow rate should be measured at intermediate points during the sampling period. Ideally, a rotameter should be included to allow observation of the flow rate without interruption of the sampling process.

10.4 To collect an air sample, the midget impingers are loaded with 10 mL each of sampling reagent. The impingers are installed in the sampling system and sample flow is started. The following parameters are recorded on the data sheet (see Figure 3 for an example): date, sampling location, time, ambient temperature, barometric pressure (if available), relative humidity (if available), dry gas meter reading (if appropriate), flow rate, rotameter setting, sampling reagent batch number, and dry gas meter and pump identification numbers.

10.5 The sampler is allowed to operate for the desired period, with periodic recording of the variables listed above. The total flow should not exceed 50 L. If it does, the operator must use a second impinger.

10.6 At the end of the sampling period, the parameters listed in Section 10.4 are recorded and the sample flow is stopped. If a dry gas meter is not used, the flow rate must be checked at the end of the sampling interval. If the flow rates at the beginning and end of the sampling period differ by more than 15%, the sample should be marked as suspect.

10.7 Immediately after sampling, the impinger is removed from the sampling system. The contents of the impinger are emptied into a clean 20-mL glass vial with a Teflon-lined screw cap. The impinger is then rinsed with 2-3 mL of toluene and the rinse solution is added to the vial. The vial is then capped, sealed with Teflon tape, and placed in a friction-top can containing 1-2 inches of granular charcoal. The samples are stored in the can and refrigerated until analysis.

10.8 If a dry gas meter or equivalent total flow indicator is not used, the average sample flow rate must be calculated according to the following equation:

$$Q_A = \frac{Q_1 + Q_2 \cdots\cdot Q_N}{N}$$

where

Q_A = average flow rate (mL/minute).

$Q_1, Q_2 \ldots . Q_N$ = flow rates determined at the beginning, end, and intermediate points during sampling.

N = number of points averaged.

10.9 The total flow is then calculated using the following equation:

$$V_m = \frac{(T_2 - T_1)Q_A}{1000}$$

where

V_m = total sample volume (L) at measured temperature and pressure.

T_2 = stop time.

T_1 = start time.

$T_1 - T_2$ = total sampling time (minutes).

Q_a = average flow rate (mL/minute).

11. Sample Analysis

11.1 Sample Preparation

11.1.1 The samples are returned to the laboratory in 20-ml screw-capped vials and refrigerated in charcoal containing cans until analysis.

11.1.2 The sample vial is placed in an aluminum heating block maintained at 60°C and a gentle stream of pure nitrogen gas is directed across the sample.

11.1.3 When the sample reaches complete dryness, the vial is removed from the heating block, capped, and cooled to near room temperature. A 1-mL volume of HPLC mobile phase (50/50 acetonitrile/water) is placed in the vial. The vial is then capped and gently shaken to dissolve the residue.

11.1.4 The concentrated sample is then refrigerated until HPLC analysis, as described in Section 11.2.

11.2 HPLC Analysis

11.2.1 The HPLC system is assembled and calibrated as described in Section 12. The operating parameters are as follows:

Column:	C-18 RP
Mobile Phase:	30% acetonitrile/70% distilled water
Detector:	ultraviolet, operating at 254 nm
Flow Rate:	1 mL/min

Before each analysis, the detector baseline is checked to ensure stable operation.

11.2.2 A 25-uL aliquot of the sample, dissolved in HPLC mobile phase, is drawn into a clean HPLC injection syringe. The sample injection loop is loaded and an injection is made. The data system is activated simultaneously with the injection and the point of injection is marked on the strip-chart recorder.

11.2.3 After approximately one minute, the injection valve is returned to the "load" position and the syringe and valve are flushed with mobile phase in preparation for the next sample analysis.

11.2.4 After elution of carbanilide, data acquisition is terminated and the component concentrations are calculated as described in Section 13.

11.2.5 Once a stable baseline is achieved, the system can be used for further sample analyses as described above.

11.2.6 If the concentration of carbanilide exceeds the linear range of the instruments, the sample should be diluted with mobile phase, or a smaller volume can be injected into the HPLC.

11.2.7 If the retention time is not duplicated, as determined by the calibration curve, you may increase or decrease the acetonitrile/water ratio to obtain the correct elution time, as specified in Figure 4. If the elution time is too long, increase the ratio; if it is too short, decrease the ratio.

11.2.8 If a dirty column causes improper detection of carbanilide, you may reactivate the column by reverse solvent flushing utilizing the following sequence: water, methanol, acetonitrile, dichloromethane, hexane, acetonitrile, then 50/50 acetonitrile in water.

12. HPLC Assembly and Calibration

12.1 The HPLC system is assembled and operated according to the parameters outlined in Section 11.2.1. An example of a typical chromatogram oabtained using the above parameters is shown in Figure 4.

12.2 The mobile phase is prepared by mixing 500 mL of acetonitrile and 500 mL of reagent water. This mixture is filtered through a 0.22-um polyester membrane filter in an all-glass and Teflon suction filtration. A constant back pressure restrictor (50 psi) or short length (6-12 inches) of 0.01-inch I.D. Teflon tubing should be placed after the detector to eliminate further mobile phase outgassing.

12.3 The mobile phase is placed in the HPLC solvent reservoir and the pump is set at a flow rate of 1 mL/minute and allowed to pump for 20-30 minutes before the first analysis. The detector is switched on at least 30 minutes before the first analysis and the detector output is displayed on a strip-chart recorder or similar output device at a sensitivity of ca 0.008 absorbance units full scale (AUFS). Once a stable baseline is achieved, the system is ready for calibration.

12.4 Carbanilide standards are prepared in HPLC mobile phase. A concentrated stock solution of 100 mg/L is prepared by dissolving 10 mg of carbanilide in 100 mL of mobile phase. This solution is used to prepare calibration standards containing concentrations of 0.05-5 mg/L.

12.5 Each calibration standard (at least five levels) is analyzed three times and area response is tabulated against mass injected. All calibration runs are performed as described for sample analyses in Section 11. Using the UV detector, a linear response range (Figures 5a through 5e) of approximately 0.1 to 10 mg/L should be achieved for a 25-uL injection volumes. The results may be used to prepare a calibration curve, as illustrated in Figure 6. Linear response is indicated where a correlation coefficient of at least 0.999 for a linear least-squares fit of the data (concentration versus area response) is obtained.

12.6 Once linear response has been documented, an intermediate concentration standard near the anticipated levels for ambient air, but at least 10 times the detection limit, should be chosen for daily calibration. The response for carbanilide should be within 10% day to day. If greater variability is observed, more frequent calibration may be required to ensure that valid results are obtained or a new calibration curve must be developed from fresh standards.

12.7 The response for carbanilide in the daily calibration standard is used to calculate a response factor according to the following equation:

$$RF_c = \frac{C_c \times V_I}{R_c}$$

where

RF_c = response factor (usually area counts) for carbanilide in nanograms injected/response unit.

C_c = concentration (mg/L) of carbanilide in the daily calibration standard.

V_I = volume (uL) of calibration standard injected.

R_c = response (area counts) for carbanilide in calibration standard.

13. Calculations

13.1 The volume of air sampled is often reported uncorrected for atmospheric conditions (i.e., under ambient conditions). The value should be adjusted to standard conditions (25°C and 760 mm pressure) using the following equation:

$$V_s = V_m \times \frac{P_A}{760} \times \frac{298}{273 + T_A}$$

where

V_s = total sample volume (L) at 25°C and 760 mm Hg pressure.

V_m = total sample volume (L) under ambient conditions, calculated as in Section 10.9 or from dry gas meter reading.

P_A = ambient pressure (mm Hg).

T_A = ambient temperature (°C).

13.2 The concentration of carbanilide is calculated for each sample using the following equation:

$$W_d = RF_c \text{ X } R_d \text{ X } \frac{V_E}{V_I}$$

where

W_d = total quantity of carbanilide (ug) in the sample.
RF_c = response factor calculated in Section 12.7.
R_d = response (area counts or other response units) for carbanilide in sample extract.
V_E = final volume (mL) of sample extract.
V_I = volume (uL) of extract injected into the HPLC system.

13.3 The concentration of phosgene in the original sample is calculated from the following equation:

$$C_A = \frac{W_d}{V_m \text{ (or } V_s)} \times \frac{99}{212} \times 1000$$

where

C_A = concentration of phosgene (ng/L)in the original sample.
W_d = total quantity of carbanilide (ug) in sample.
V_m = total sample volume (L) under ambient conditions.
V_c = total sample volume (L) at 25 ^{o}C and 760 mm Hg.
$\frac{99}{212}$ = the molecular weights (g/mole) of phosgene and carbanilide are 99 and 212 g/mole, respectively.

13.4 The phosgene concentrations can be converted to ppbv using the following equation:

$$C_A\ (\text{ppbv}) = C_A\ (\text{ng/L}) \times \frac{24.4}{99}$$

where

C_A (ng/L) is calculated using V_s.

14. Performance Criteria and Quality Assurance

This section summarizes required quality assurance (QA) measures and provides guidance concerning performance criteria that should be achieved within each laboratory.

14.1 Standard Operating Procedures (SOPs).

14.1.1 Users should generate SOPs describing the following activities in their laboratory: 1) assembly, calibration, and operation of the sampling system with make and model of equipment used; 2) preparation, purification, storage, and handling of sampling reagent and samples; 3) assembly, calibration, and operation of the HPLC system with make and model of equipment used; and 4) all aspects of data recording and processing, including lists of computer hardware and software used.

14.1.2 SOPs should provide specific stepwise instructions and should be readily available to and understood by the laboratory personnel conducting the work.

14.2 HPLC System Performance

14.2.1 The general appearance of the HPLC chromatogram should be similar to that illustrated in Figure 4.

14.2.2 The HPLC system efficiency and peak asymmetry factor should be determined in the following manner:

A solution of carbanilide corresponding to at least 20 times the detection limit should be injected with the recorder chart sensitivity and speed set to yield a peak approximately 75% of full scale and 1 cm wide at half height. The peak asymmetry factor is determined as shown in Figure 7, and should be between 0.8 and 1.8.

14.2.3 HPLC system efficiency is calculated according to the following equation:

$$N = 5.54 \frac{t_r}{W_{1/2}}$$

where

N = column efficiency (theoretical plates).
t_r = retention time (seconds) of carbanilide.
$W_{1/2}$ = width of component peak at half height (seconds).

A column efficiency of >5,000 theoretical plates should be obtained.

14.2.4 Precision of response for replicate HPLC injections should be ±10% or less, day to day, for calibration standards. Precision of retention times should be ±2%, on a given day.

14.3 Process Blanks

14.3.1 Before use, a 10-mL aliquot of each batch of sampling reagent should be analyzed as described in Section 11. The blank should contain less than 50 ng of carbanilide per 10-mL aliquot.

14.3.2 At least one field blank or 10% of the field samples, whichever is larger, should be shipped and analyzed with each group of samples. The field blank is treated identically to the samples except that no air is drawn through the reagent. The same performance criteria described in Section 14.3.1 should be met for process blanks.

14.4 Method Precision and Recovery

14.4.1 Analysis of replicate samples indicates that a precision of ±15-20% relative standard deviation can be readily achieved (see Table 1). Each laboratory should collect parallel samples periodically (at least one for each batch of samples) to document its precision in conducting the method.

14.4.2 Precision for replicate HPLC injections should be ±10% or better, day to day, for calibration standards.

14.4.3 Before using the method in the field, each laboratory must confirm the performance of the method under its particular conditions. Since static, dilute, gas phase standards of phosgene are unstable, a dynamic flow/permeation tub system should be assembled as described in the literature(1). ASTM Method D 3609(3) should be used as the protocol for operating such a system.

14.4.4 Once a suitable dynamic flow/permeation tube system has been constructed, a series of three samples from the outlet gas stream (60 L) should be sampled at three different spike levels (achieved by adjusting the air flow through the permeation chamber). Precision and recovery data comparable to those shown in Table 1 should be achieved.

REFERENCES

1. Spicer, C. W., R. M. Riggin, M. W. Holdren, F. L. DeRoos, and R. N. Lee, Atmospheric Reaction Products from Hazardous Air Pollutants, Final Report on Contract 68-02-3169 (WA-33/40), U.S. Environmental Protection Agency, Research Triangle Park, N.C., July, 1984.

2. Method 219, "Phosgene in Air," Manual of Analytical Methods, National Institute for Occupational Safety and Health.

3. Annual Book of ASTM Standards, Part 11.03, "Atmospheric Analysis," American Society for Testing and Materials, Philadelphia, Pennsylvania, 1983.

4. Riggin, R. M., "Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air," EPA-600/4-83-027. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1983.

5. "Method 6 Determination of SO_2 Emissions from Stationary Sources," Federal Register, Vol. 42., No. 160, August, 1977.

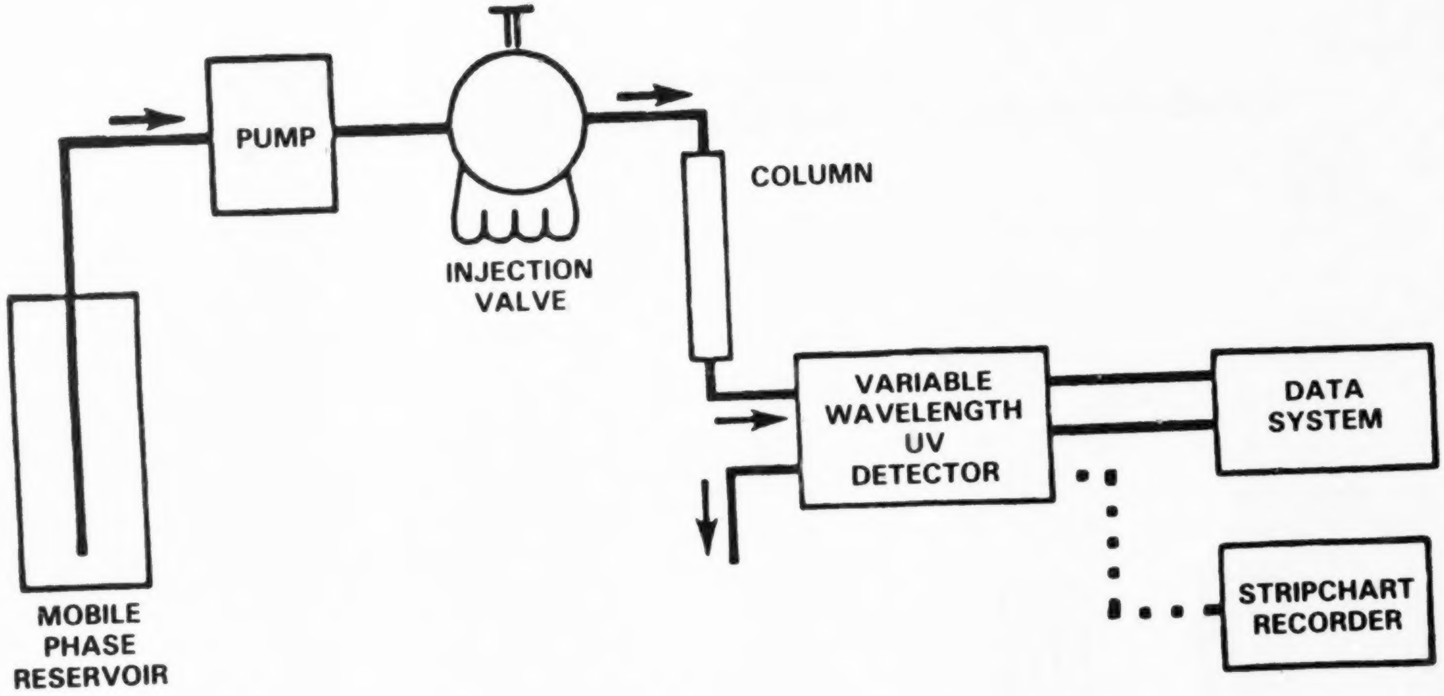

PUMP
COLUMN
INJECTION VALVE
VARIABLE WAVELENGTH UV DETECTOR
DATA SYSTEM
STRIPCHART RECORDER
MOBILE PHASE RESERVOIR

FIGURE 1. TYPICAL HPLC SYSTEM

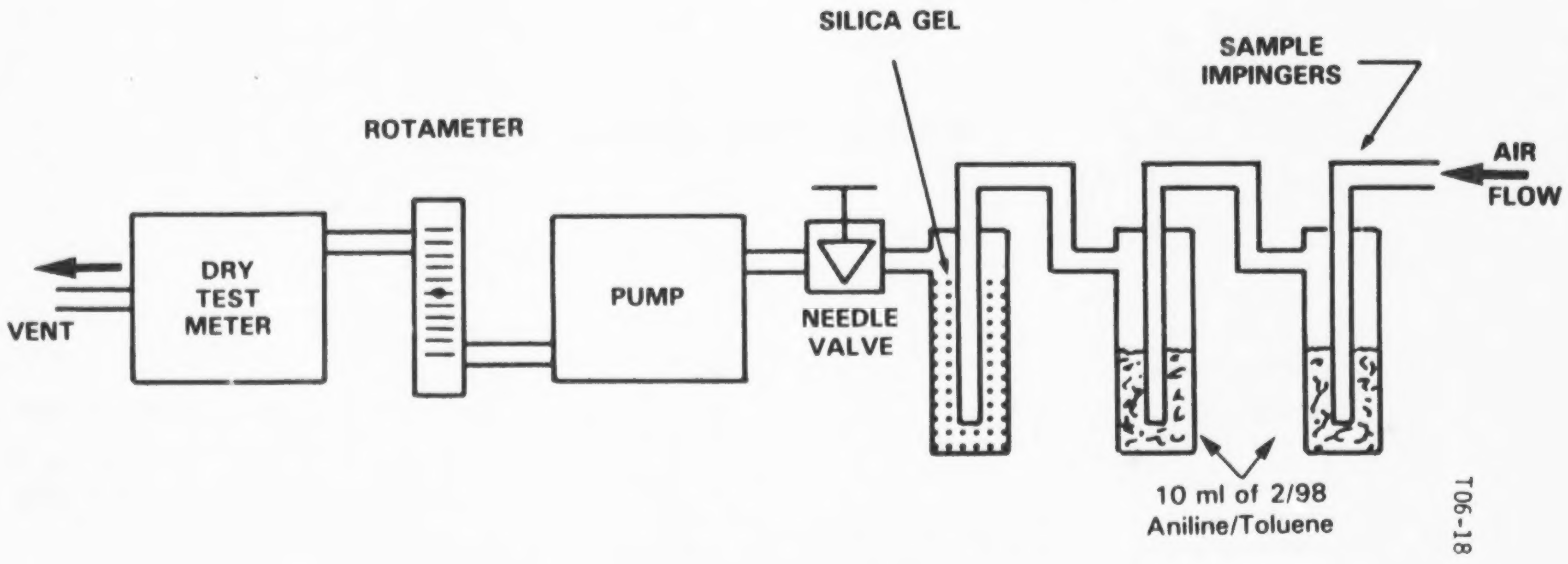

SILICA GEL
SAMPLE IMPINGERS
ROTAMETER
AIR FLOW
DRY TEST METER
PUMP
VENT
NEEDLE VALVE
10 ml of 2/98 Aniline/Toluene
T06-18

FIGURE 2. TYPICAL SAMPLING SYSTEM FOR MONITORING PHOSGENE IN AMBIENT AIR

SAMPLING DATA SHEET
(One Sample per Data Sheet)

PROJECT: ____________________

SITE: ____________________

LOCATION: ____________________

INSTRUMENT MODEL NO: __________

PUMP SERIAL NO: __________

DATES(S) SAMPLED: ____________________

TIME PERIOD SAMPLED: ____________________

OPERATOR: ____________________

CALIBRATED BY: ____________________

SAMPLING DATA

Sample Number: ____________________

Start Time: __________ Stop Time: __________

Time	Dry Gas Meter Reading	Rotameter Reading	Flow Rate,*Q mL/min	Ambient Temperature °C	Barometric Pressure, mm Hg	Relative Humidity, %	Comments
1.							
2.							
3.							
4.							
N.							

Total Volume Data**

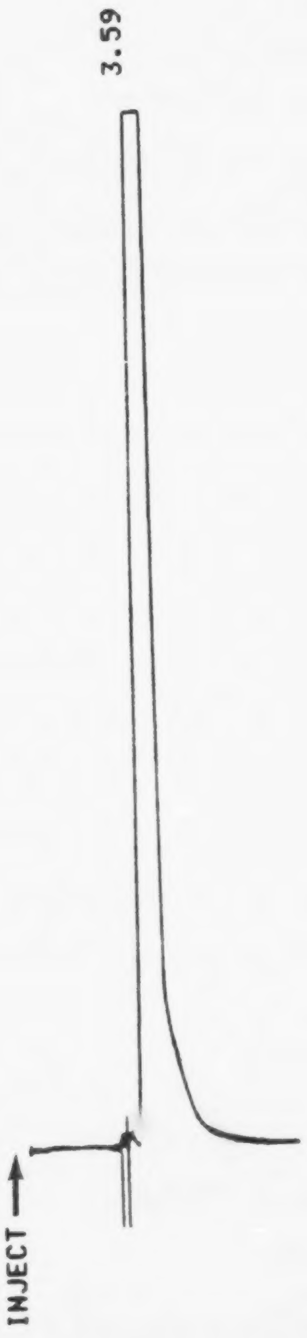
V_m = (Final - Initial) Dry Gas Meter Reading, or = ______ L

$$= \frac{Q_1 + Q_2 + Q_3 \cdots Q_N}{N} \times \frac{1}{1000 \times (\text{Sampling Time in Minutes})} = \_\_\_\_\_\_ \text{ L}$$

* Flow rate from rotameter or soap bubble calibrator (specify which).

** Use data from dry gas meter if available.

FIGURE 3. TYPICAL SAMPLING DATA FORM



OPERATING PARAMETERS
HPLC

Column: C-18 RP
Mobile Phase: 30% Acetonitrile/70% Distilled Water
Detector: Ultra violet operating at 254 nm
Flow Rate: 1 ml/min
Retention Time: 3.59 minutes

```
AUG. 22. 1986   15.25.17  CHART 0.50 CM/MIN
                          RUN #50    CALC #0
                          SOLVENT   OPR ID                    3
COLUMN

EXTERNAL STANDARD QUANTITATION

PEAK#        AMOUNT    RT    EXP RT          AREA          RF
            2.75300   2.74                 2753 L   0.000000E0
        10020.20000   3.59             10020345 L   0.000000E0
TOTAL   10023.00000
```

FIGURE 4. CHROMATOGRAM FOR 3 ppbv OF PHOSGENE SPIKED INTO CLEAN AIR

OPERATING PARAMETERS
HPLC

Column: C-18 RP
Mobile Phase: 30% Acetonitrile/70% Distilled Water
Detector: Ultra violet operating at 254 nm
Flow Rate: 1 ml/min
Retention Time: 3.59 minutes

CONC	AREA COUNTS
1μg	2126577
2μg	4243289
3μg	6312128
4μg	8373790
5μg	10020345

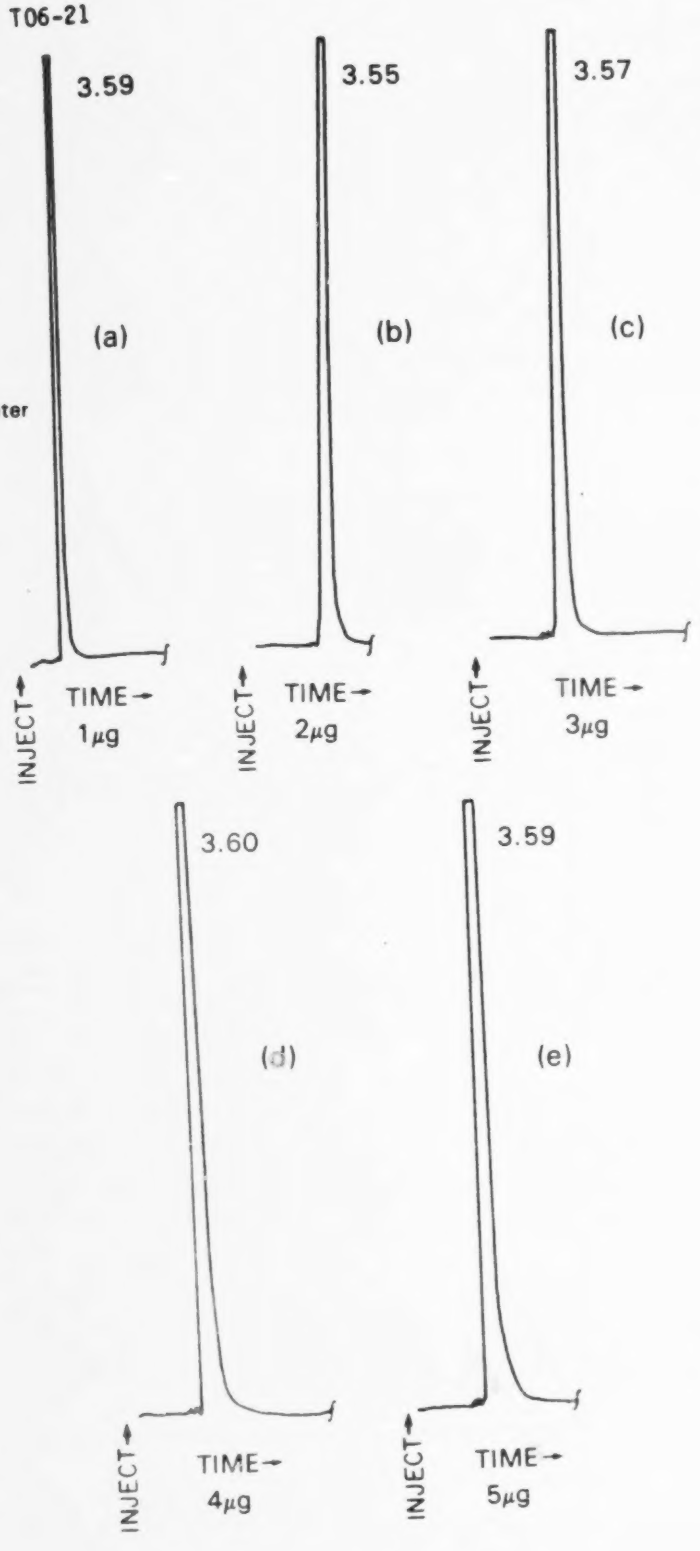
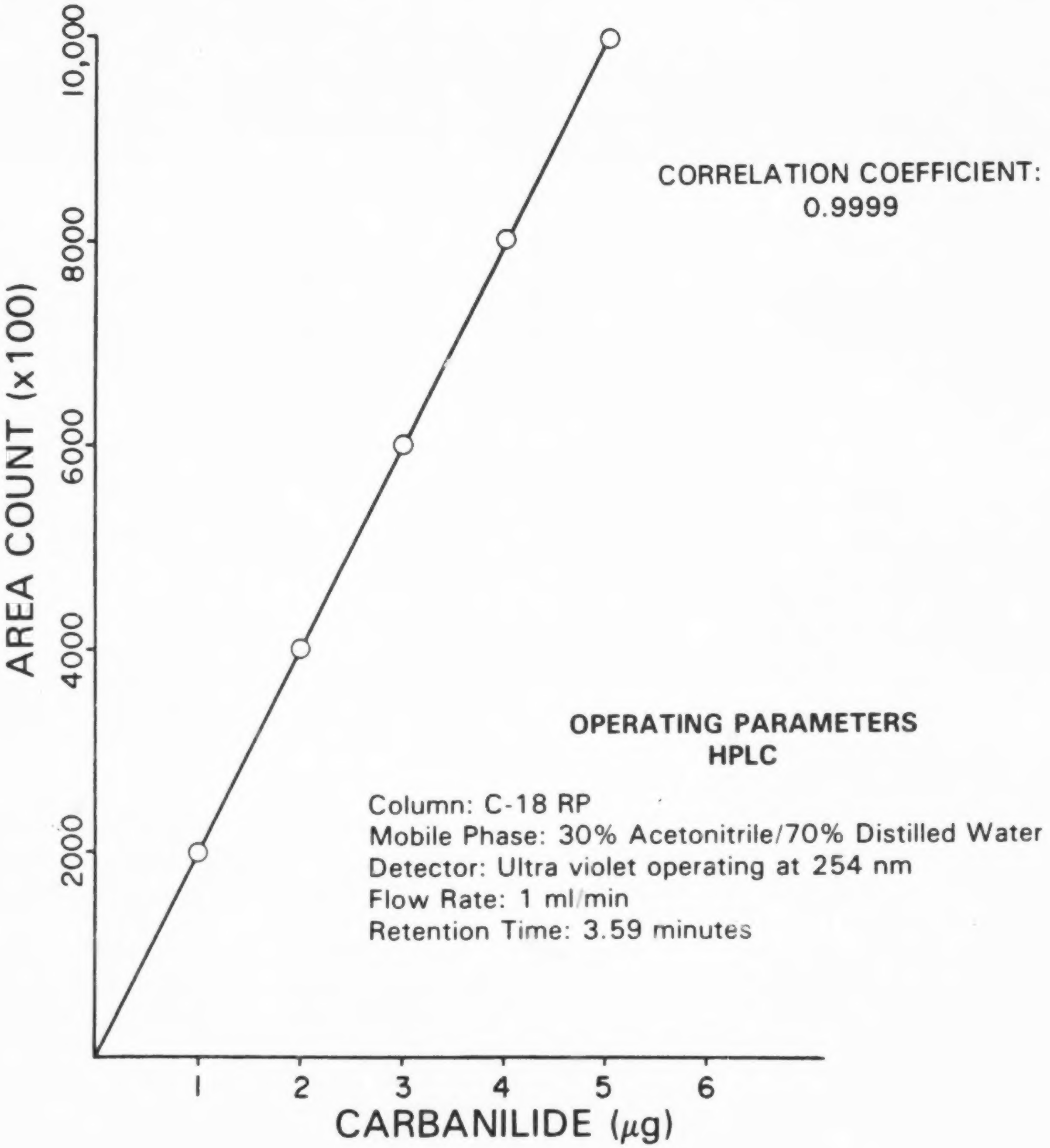


FIGURE 5a-5e. HPLC CHROMATOGRAM OF VARYING CARBANILIDE CONCENTRATIONS

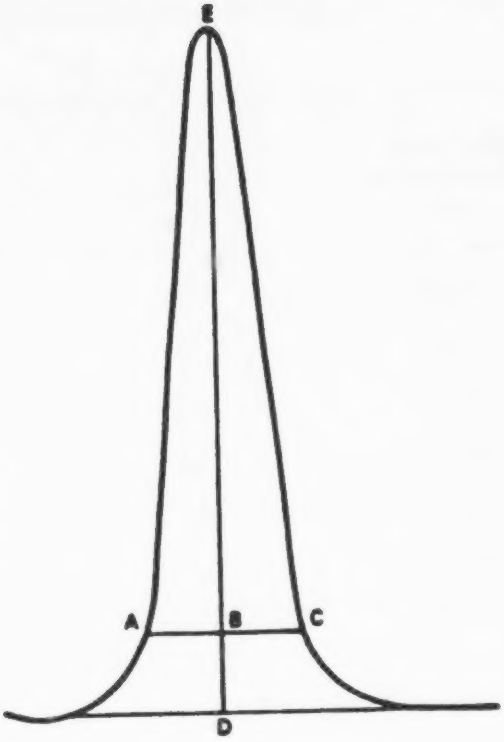


CORRELATION COEFFICIENT:
0.9999

OPERATING PARAMETERS
HPLC

Column: C-18 RP
Mobile Phase: 30% Acetonitrile/70% Distilled Water
Detector: Ultra violet operating at 254 nm
Flow Rate: 1 ml/min
Retention Time: 3.59 minutes

FIGURE 6. CALIBRATION CURVE FOR CARBANILINE



$$\text{Asymmetry Factor} = \frac{BC}{AB}$$

Example Calculation:
Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm

$$\text{Therefore: Asymmetry Factor} = \frac{12}{11} = 1.1$$

FIGURE 7. PEAK ASYMMETRY CALCULATION

TABLE 1: PRECISION AND RECOVERY DATA FOR PHOSGENE IN CLEAN AIR

Phosgene Concentration, ppbv	Recovery, %	Standard Deviation
0.034	63	13
0.22	87	14
3.0	99	3
4.3	109	12
20	99	14
200	96	7

Revision 1.0
September, 1986

METHOD TO7 - 1

METHOD FOR THE DETERMINATION OF N-NITROSODIMETHYLAMINE IN AMBIENT AIR USING GAS CHROMATOGRAPHY

1. Scope

1.1 This document describes a method for determination of N-nitrosodimethylamine (NDMA) in ambient air. Although the method, as described, employs gas chromatography/mass spectrometry (GC/MS), other detection systems are allowed.

1.2 Although additional documentation of the performance of this method is required, a detection limit of better than 1 ug/m^3 is achievable using GC/MS (1,2). Alternate, selective GC detection systems such as a thermal energy analyzer (2), a thermionic nitrogen-selective detector (3), or a Hall Electrolytic conductivity detector (4) may prove to be more sensitive and selective in some instances.

2. Applicable Documents

2.1 ASTM Standards
D1356 Definitions of Terms Related to Atmospheric Sampling and Analysis (5)

2.2 Other Documents
Ambient air studies (1,2)
U.S. EPA Technical Assistance Document (6)

3. Summary of Method

3.1 Ambient air is drawn through a Thermosorb/N adsorbent cartridge at a rate of approximately 2 L per minute for an appropriate period of time. Breakthrough has been shown not to be a problem with total sampling volumes of 300 L (i.e., 150 minutes at 2 L per minute). The selection of Thermosorb/N absorbent over Tenax GC, was due, in part, to recent laboratory studies indicating artifact formation on Tenax from the presence of oxides of nitrogen in the sample matrix.

3.2 In the laboratory, the cartridges are pre-eluted with 5 mL of dichloromethane (in the same direction as sample flow) to remove interferences. Residual dichloromethane is removed by purging the cartridges with air in the same direction. The cartridges are then eluted, in the reverse direction, with 2 mL of acetone. This eluate is collected in a screw-capped vial and refrigerated until analysis.

3.3 NDMA is determined by GC/MS using a Carbowax 20M capillary column. NDMA is quantified from the response of the m/e 74 molecular ion using an external standard calibration method.

4. Significance

4.1 Nitrosamines, including NDMA, are suspected human carcinogens. These compounds may be present in ambient air as a result of direct emission (e.g., from tire manufacturing) or from atmospheric reactions between secondary or tertiary amines and NO_x.

4.2 Several papers (1,2,4) have been published describing analytical approaches for NDMA determination. The purpose of this document is to combine the attractive features of these methods into one standardized method. At the present time, this method has not been validated in its final form, and, therefore, one must use caution when employing it for specific applications.

5. Definitions

Definitions used in this document and in any user-prepared SOPs should be consistent with ASTM D1356(5). All abbreviations and symbols are defined within this document at the point of use.

6. Interferences

Compounds having retention times similar to NDMA, and yielding detectable m/e 74 ion fragments, may interfere in the method. The inclusion of a pre-elution step in the sample desorption procedure minimizes the number of interferences. Alternative GC columns and conditions may be required to overcome interferences in unique situations.

7. Apparatus

7.1 GC/MS System - capable of temperature-programmed, fused-silica capillary column operation. Unit mass resolution or better to 300 amu. Capable of full scan and selected ion monitoring with a scan rate of 0.8 second/scan or better.

7.2 Sampling system - capable of accurately and precisely sampling 100-2000 mL/minute of ambient air. (See Figure 1.) The dry test meter may not be accurate at flows below 500 mL/minute; in such cases it should be replaced by recorded flow readings at the start, finish, and hourly during the collection. See Section 9.4.

7.3 Stopwatch.

7.4 Friction top metal can, e.g., one-gallon (paint can) - to hold clean cartridges and samples.

7.5 Thermometer - to record ambient temperature.

7.6 Barometer (optional).

7.7 Glass syringe - 5 mL with Luer® fitting.

7.8 Volumetric flasks - 2 mL, 10 mL, and 100 mL.

7.9 Glass syringe - 10 uL for GC injection.

8. Reagents and Materials

8.1 Thermosorb/N - Available from Thermedics Inc., 470 Wildwood St., P.O.Box 2999, Woburn, Mass., 01888-1799, or equivalent.

8.2 Dichloromethane - Pesticide quality, or equivalent.

8.3 Helium - Ultrapure compressed gas (99.9999%).

8.4 Perfluorotributylamine (FC-43) - for GC/MS calibration.

8.5 Chemical Standards - NDMA solutions. Available from various chemical supply houses. Caution: NDMA is a suspected human carcinogen. Handle in accordance with OSHA regulations.

8.6 Granular activated charcoal - for preventing contamination of cartridges during storage.

8.7 Glass jar, 4 oz - to hold cartridges.

8.8 Glass vial - 1 dram, with Teflon®-lined screw cap.

8.9 Luer® fittings - to connect cartridges to sampling system.

8.10 Acetone- Reagent grade.

9. Sampling

9.1 Cartridges (Thermosorb/N) are purchased prepacked from Thermedics Inc. These cartridges are 1.5 cm ID x 2 cm long polyethylene tubes with Luer®-type fittings on each end. The adsorbent is held in place with 100-mesh stainless steel screens at each end. The cartridges are used as received and are discarded after use. At least one cartridge from each production lot should be used as a blank to check for contamination. The cartridges are stored in screw-capped glass jars (with Luer® style caps), and placed in a charcoal-containing metal can when not in use.

9.2 The sampling system may employ either a mass flow controller or a dry test meter. (See Figure 1.) For purposes of discussion, the following procedure assumes the use of a dry test meter.

9.3 Before sample collection, the entire assembly (including a "dummy" sampling cartridge) is installed and the flow rate is checked at a value near the desired rate. In general, flow rates of 100-2000 mL/minute should be employed. The flow rate should be adjusted so that no more than 300 L of air is collected over the desired sampling period. Generally, calibration is accomplished using a soap bubble flow meter or calibrated wet test meter connected to the flow exit, assuming the system is sealed. ASTM Method 3686 describes an appropriate calibration scheme not requiring a sealed flow system downstream of the pump.

9.4 Ideally, a dry gas meter is included in the system to record total flow. If a dry gas meter is not available, the operator must measure and record the sampling flow rate at the beginning and end of the sampling period to determine sample volume. If the sampling period exceeds two hours, the flow rate should be measured at intermediate points during the sampling period. Ideally, a rotameter should be included to allow observation of the flow rate without interruption of the sampling process.

9.5 To collect an air sample, a new Thermosorb/N cartridge is removed from the glass jar and connected to the sampling system using a Luer® adapter fitting. The glass jar is sealed for later use. The following parameters are recorded on the data sheet (see Figure 2 for an example): date, sampling location, time, ambient temperature, barometric pressure (if available), relative humidity (if available), dry gas meter reading (if appropriate), flow rate, rotameter setting, cartridge batch number, and dry gas meter and pump identification numbers.

9.6 The sampler is allowed to operate for the desired period, with periodic recording of the variables listed above. The total flow should not exceed 300 L.

9.7 At the end of the sampling period, the parameters listed in Section 9.5 are recorded and the sample flow is stopped. If a dry gas meter is not used, the flow rate must be checked at the end of the sampling interval. If the flow rates at the beginning and end of the sampling period differ by more than 15%, the sample should be marked as suspect.

9.8 Immediately after sampling, the cartridge is removed from the sampling system, capped, and placed back in the 4-oz glass jar. The jar is then capped, sealed with Teflon® tape, and placed in a friction-top can containing 1-2 inches of granular charcoal. The samples are stored in the can until analysis.

9.9 If a dry gas meter or equivalent total flow indicator is not used, the average sample flow rate must be calculated according to the following equation:

$$Q_A = \frac{Q_1 + Q_2 + \cdots Q_N}{N}$$

where

Q_A = average flow rate (mL/minute).
Q_1, Q_2, ...Q_N = flow rates determined at beginning, end, and immediate points during sampling.
N = number of points averaged.

9.10 The total flow is then calculated using the following equation:

$$V_m = \frac{(T_2-T_1) \times Q_A}{1000}$$

where

V_m = total sample volume (L) at measured temperature and pressure.
T_2 = stop time.
T_1 = start time.
T_2-T_1 = sampling time (minutes).

9.11 The total volume (V_s) at standard conditions, 25°C and 760 mm Hg, is calculated from the following equation:

$$V_s = V_m \times \frac{P_A}{760} \times \frac{298}{273 + t_A}$$

where V_s = total sample volume (L) at standard conditions of 25° C and 760 mm Hg.

V_m = total sample volume (L) at measured temperature and pressure.

P_A = average barometric pressure (mm Hg).

t_A = average ambient temperature (°C).

10. Sample Desorption

10.1 Samples are returned to the laboratory and prepared for analysis within one week of collection.

10.2 Using a glass syringe, the samples are pre-eluted to remove potential interferences by passing 5 mL of dichloromethane through the cartridge, in the same direction as sample flow. This operation should be conducted over approximately a 2-minute period. Excess solvent is expelled by injecting 5 mL of air through the cartridge, again using the glass syringe.

10.3 The NDMA is then desorbed passing 2 mL of acetone through the cartridge, in the direction opposite to sample flow, using a glass syringe. A flow rate of approximately 0.5 mL/minute is employed and the eluate is collected in a 2-mL volumetric flask.

10.4 Desorption is halted once the volumetric flask is filled to the mark. The sample is then transferred to a 1-dram vial having a Teflon®-lined screw cap and refrigerated until analysis. The vial is wrapped with aluminum foil to prevent photolytic decomposition of the NDMA.

11. GC/MS Analysis

Although a variety of GC detectors can be used for NDMA determination, the following procedure assumes the use of GC/MS in the selected ion monitoring (SIM) mode.

11.1 Instrument Setup

11.1.1 Considerable variation in instrument configuration is expected from one laboratory to another. Therefore, each laboratory must be responsible for verifying that its particular system yields satisfactory results. The GC/MS system must be capable of accommodating a fused-silica capillary column, which can be inserted directly into the ion source. The system must be capable of acquiring and processing data in the selected ion monitoring mode.

11.1.2 Although alternative column systems can be used, a 0.2 mm I.D. x 50 m Carbowax 20M fused-silica column (Hewlett-Packard Part No. 19091-60150, or equivalent) is recommended. After installation, a helium carrier gas flow of 2 mL per minute is established and the column is conditioned at 250°C for 16 hours. The injector and GC/MS transfer line temperatures should also be set at 250°C.

11.1.3 The MS and data system are set up according to manufacturer's specifications. Electron impact ionization (70 eV) should be employed. Once the entire GC/MS system is set up, it is calibrated as described in Section 11.2. The user should prepare a detailed standard operating procedure (SOP) describing this process for the particular instrument being used.

11.2 Instrument Calibration

11.2.1 Tuning and mass standardization of the MS system is performed according to manufacturer's instructions and relevant information from the user-prepared SOP. Perfluorotributylamine should generally be employed for this purpose. The material is introduced directly into the ion source through a molecular leak. The instrumental parameters (e.g., lens, voltages, resolution, etc.) should be adjusted to give the relative ion abundances shown in Table 1 as well as acceptable resolution and peak shape. If these approximate relative abundances cannot be achieved, the ion source may require cleaning according to manufacturer's instructions. In the event that the user's instrument cannot achieve these relative ion abundances, but is otherwise operating properly, the user may adopt another set of relative abundances as performance criteria. However, these values must be repeatable on a day-to-day basis.

11.2.2 After the mass standardization and tuning process has been completed and the appropriate values entered into the data system, the user should set the SIM monitoring parameters (i.e., mass centroid and window to be monitored) by injecting a moderatley high level standard solution (100 ug/mL) of NDMA onto the GC/MS in the full scan mode. The scan range should be 40 to 200 amu at a rate of 0.5 to 0.8 scans/second. The nominal mass 42, 43, and 74 amu ions are to be used for SIM monitoring, with the 74 amu ion employed for NDMA quantification.

11.2.3 Before injection of NDMA standards, the GC oven temperature is stabilized at 45°C. The filament and electron multiplier voltage are turned off. A 2-uL aliquot of an appropriate NDMA standard, dissolved in acetone, is injected onto the GC/MS system using the splitless injection technique. Concentrated NDMA standards can be purchased from chemical supply houses. The standards are diluted to the appropriate concentration with acetone. CAUTION: NDMA is a suspected carcinogen and must be handled according to OSHA regulations. After five minutes, the electron multiplier and filament are turned on, data acquisition is initiated, and the oven temperature is programmed to 250°C at a rate of 16°C/minute. After elution of the NDMA peak from the GC/MS (Figure 3), the data acquisition process can be halted and data processing initiated.

11.2.4 Once the appropriate SIM parameters have been established, as described in Section 11.2.2, the instrument is calibrated by analyzing a range of NDMA standards using the SIM prodecure. If necessary, the electron multiplier voltage or amplifier gain can be adjusted to give the desired sensitivity for standards bracketing the range of interest. A calibration curve of m/e 74 ion intensity versus quantity of NDMA injected is constructed and used to calculate NDMA concentration in the samples.

11.3 Sample Analysis

11.3.1 The sample analysis process is the same as that described in Section 11.2.3 for calibration standards. Samples should be handled so as to minimize exposure to light.

11.3.2 If a peak is observed for NDMA (within ±6 seconds of the expected retention time), the areas (integrated ion intensities) for m/e 42, 43, and 74 are calculated. The area of the m/e 74 peak is used to calculate NDMA concentration. The ratios of m/e 42/74 and 43/74 ion intensities are used to determine the certainty of the NDMA identification. Ideally, these ratios should be within ±20% of the ratios for an NDMA standard in order to have confidence in the peak identification. Figure 4 illustrates the MS scan for N-nitrosodimethylamine.

12. Calculations

12.1 Calibration Response Factors

12.1.1 Data from calibration standards are used to calculate a response factor for NDMA. Ideally, the process involves analysis of at least three calibration levels of NDMA during a given day and determination of the response factor (area/ng injected) from the linear least squares fit of a plot of nanograms injected versus area (for the m/e 74 ion). In general, quantities of NDMA greater than 1000 nanograms should not be injected because of column overloading and/or MS response nonlinearity.

12.1.2 If substantial nonlinearity is present in the calibration curve, a nonlinear least squares fit (e.g., quadratic) should be employed. This process involves fitting the data to the following equation:

$$Y = A + BX + CX^2$$

where

Y = peak area

X = quantity of NDMA (ng)

A, B, and C are coefficients in the equation

12.2 NDMA Concentration

12.2.1 Analyte quantities on a sample cartridge are calculated from the following equation:

$$Y_A = A + BX_A + CX_A^2$$

where

Y_A is the area of the m/e 74 ion for the sample injection.

X_A is the calculated quantity of NDMA (ng) on the sample cartridge.

A, B, and C are the coefficients calculated from the calibration curve described in Section 12.1.2.

12.2.2 If instrumental response is essentially linear over the concentration range of interest, a linear equation ($C=0$ in the equation above) can be employed.

12.2.3 Concentration of analyte in the original air sample is calculated from the following equation:

$$C_A = \frac{X_A}{V_s}$$

where

C_A is the calculated concentration of analyte (ng/L).

V_s and X_A are as previously defined in Sections 9.11 and 12.2.1, respectively.

13. Performance Criteria and Quality Assurance

This section summarizes required quality assurance (QA) measures and provides guidance concerning performance criteria that should be achieved within each laboratory.

13.1 Standard Operating Procedures (SOPs).

13.1.1 User should generate SOPs describing the following activites in their laboratory: 1) assembly, calibration, and operation of the sampling system with make and model of equipment used; 2) preparation, purification, storage, and handling of Thermosorb/N cartridges and samples; 3) assembly, calibration, and operation of the GC/MS system with make and model of equipment used; and 4) all aspects of data recording and processing, including lists of computer hardware and software used.

13.1.2 SOPs should provide specific stepwise instructions and should be readily available to and understood by the laboratory personnel conducting the work.

13.2 Sample Collection

13.2.1 During each sampling event, at least one clean cartridge will accompany the samples to the field and back to the laboratory, having been placed in the sampler but without sampling air, to serve as a field blank. The average amount of material found on the field blank cartridges may be subtracted from the amount found on the actual samples. However, if the blank level is greater than 25% of the sample amount, data for that component must be identified as suspect.

13.2.2 During each sampling event, at least one set of parallel samples (two or more samples collected simultaneously) should be collected. If agreement between parallel samples is not generally within ±25%, the user should collect parallel samples on a much more frequent basis (perhaps for all sampling points).

13.2.3 Backup cartridges (two cartridges in series) should be collected with each sampling event. Backup cartridges should contain less than 10% of the amount of NDMA found in the front cartridges, or be equivalent to the blank cartridge level, whichever is greater.

13.2.4 NDMA recovery for spiked cartridges (using a solution-spiking technique) should be determined before initial use of the method on real samples. Currently available information indicates that a recovery of 75% or greater should be achieved.

13.3 GC/MS Analysis

13.3.1 Performance criteria for MS tuning and mass standardization are discussed in Section 11.2 and Table 1. Additional criteria can be used by the laboratory, if desired. The following sections provide performance guidance and suggested criteria for determining the acceptability of the GC/MS system.

13.3.2 Chromatographic efficiency should be evaluated daily by the injection of NDMA calibration standards. The NDMA peak should be plotted on an expanded time scale so that its width at 10% of the peak height can be calculated, as shown in Figure 5. The width of the peak at 10% height should not exceed 10 seconds. More stringent criteria may be required for certain applications. The asymmetry factor (see Figure 5) should be between 0.8 and 2.0.

13.3.3 The detection limit for NDMA is calculated from the data obtained for calibration standards. The detection limit is defined as

$$DL = A + 3.3S$$

where

DL is the calculated detection limit in nanograms injected.

A is the intercept calculated in Section 12.1.2.

S is the standard deviation of replicate determinations of the lowest-level standard (at least three such determinations are required). The lowest-level standard should yield a signal-to-noise ratio (from the total ion current response) of approximately 5.

13.3.4 Replicate GC/MS analysis of NDMA standards and/or sample extracts should be conducted on a daily basis. A precision of ±15% RSD or better should be achieved.

REFERENCES

(1) Marano, R. S., Updegrove, W. S., and Machem, R. C., "Determination of Trace Levels of Nitrosamines in Air by Gas Chromatography/Low Resolution Mass Spectrometry," Anal. Chem., 54, 1947-1951 (1982).

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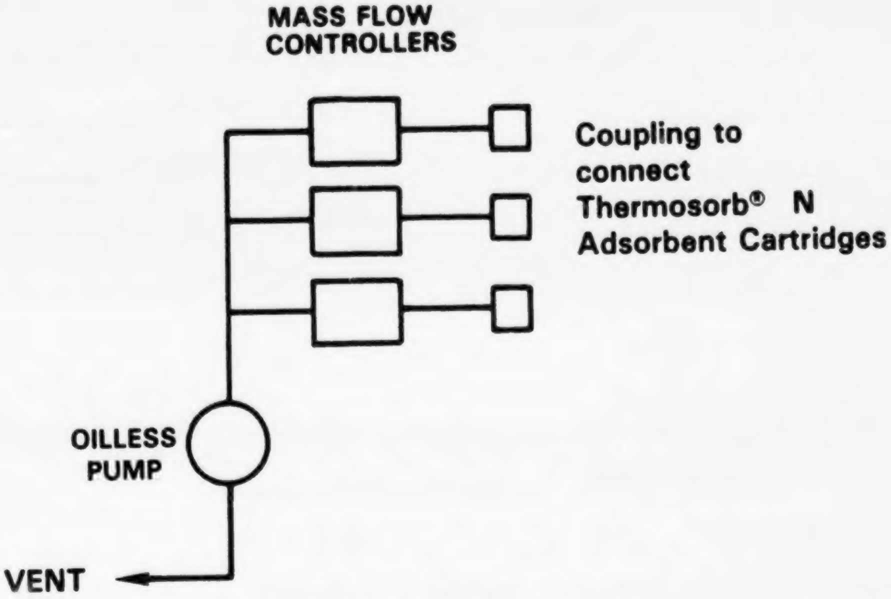
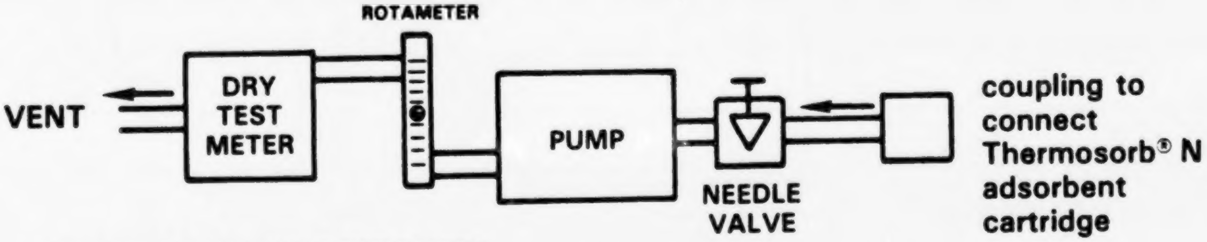
(6) Riggin, R. M., "Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air," EPA-600/4-83-027, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1983.


MASS FLOW CONTROLLERS
Coupling to connect Thermosorb® N Adsorbent Cartridges
OILLESS PUMP
VENT

(a) MASS FLOW CONTROL


ROTAMETER
VENT
DRY TEST METER
PUMP
NEEDLE VALVE
coupling to connect Thermosorb® N adsorbent cartridge

(DRY TEST METER SHOULD NOT BE USED FOR FLOW OF LESS THAN 500 ml/minutes)

(b) NEEDLE VALVE/DRY TEST METER

FIGURE 1. TYPICAL SAMPLING SYSTEM CONFIGURATION

SAMPLING DATA SHEET
(One Sample per Data Sheet)

PROJECT: ____________________

DATES(S) SAMPLED: ____________________

SITE: ____________________

TIME PERIOD SAMPLED: ____________________

LOCATION: ____________________

OPERATOR: ____________________

INSTRUMENT MODEL NO: ____________________

CALIBRATED BY: ____________________

PUMP SERIAL NO: ____________________

SAMPLING DATA

Sample Number: ____________________

Start Time: ____________ Stop Time: ____________

Time	Dry Gas Meter Reading	Rotameter Reading	Flow Rate,*Q mL/min	Ambient Temperature °C	Barometric Pressure, mm Hg	Relative Humidity, %	Comments
1.							
2.							
3.							
4.							
N.							

Total Volume Data**

V_m = (Final - Initial) Dry Gas Meter Reading, or = ______ L

$$= \frac{Q_1 + Q_2 + Q_3 \cdots Q_N}{N} \times \frac{1}{1000 \times (\text{Sampling Time in Minutes})}$$ = ______ L

* Flow rate from rotameter or soap bubble calibrator (specify which).

** Use data from dry gas meter if available.

FIGURE 2. EXAMPLE SAMPLING DATA SHEET

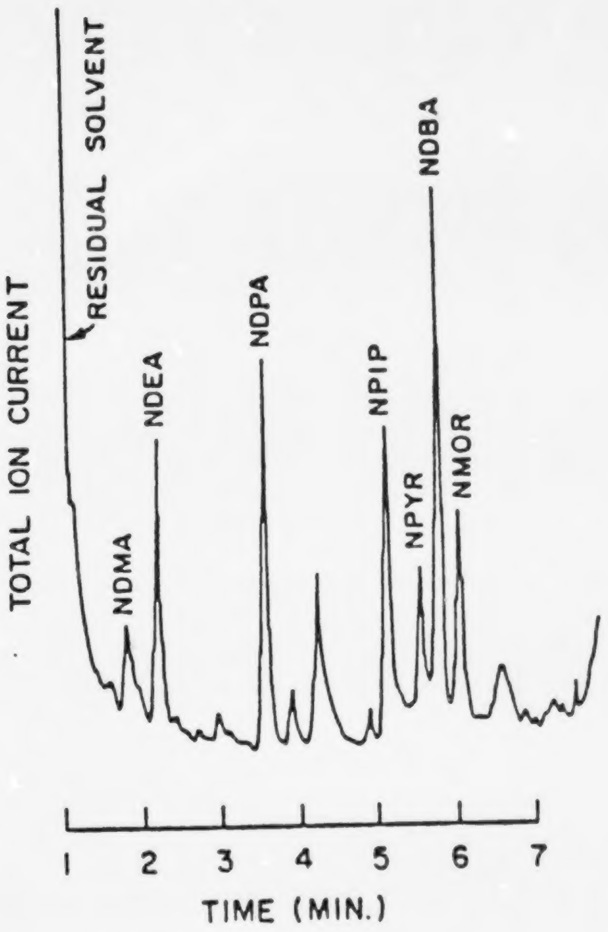


FIGURE 3. TOTAL ION CURRENT CHROMATOGRAM RESULTING FROM INJECTION OF 15 μL SAMPLE OF NDMA STANDARD (10 NG/μL IN ETHANOL).

$C_2H_6N_2O$
Methanamine, *N*—methyl—*N*—nitroso—

Me ₂ NNO

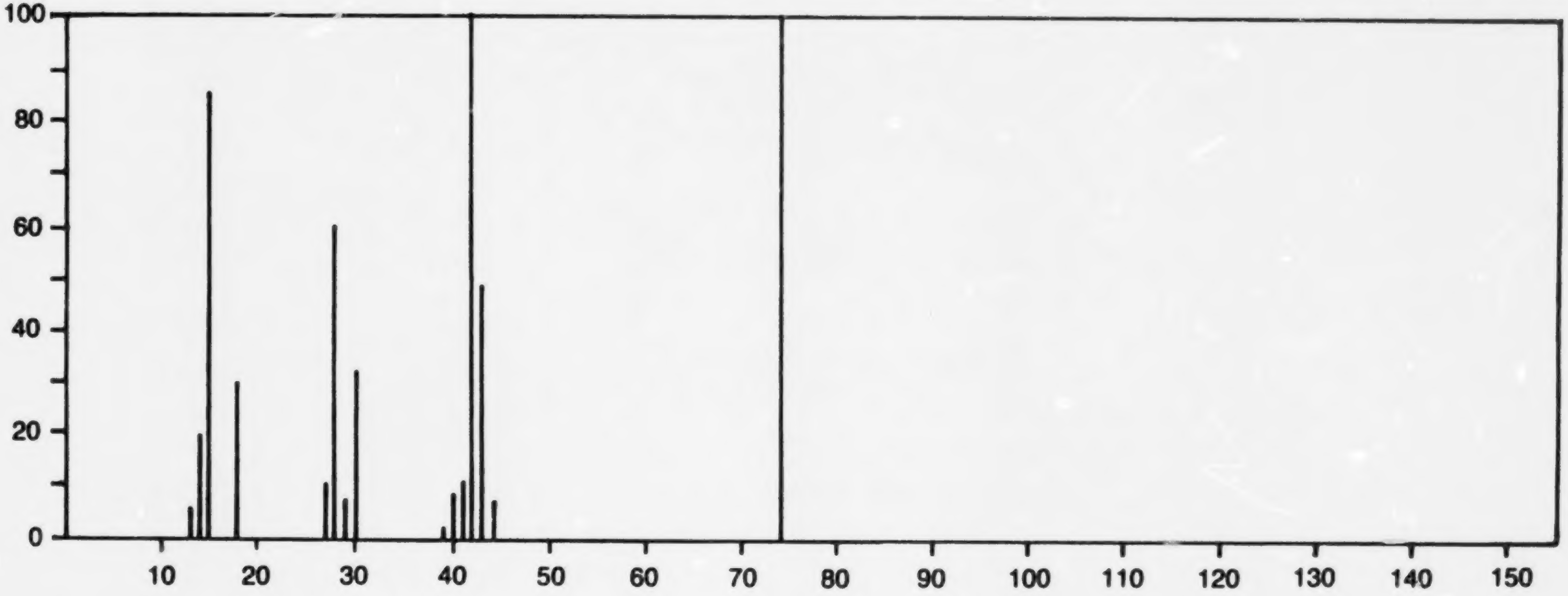
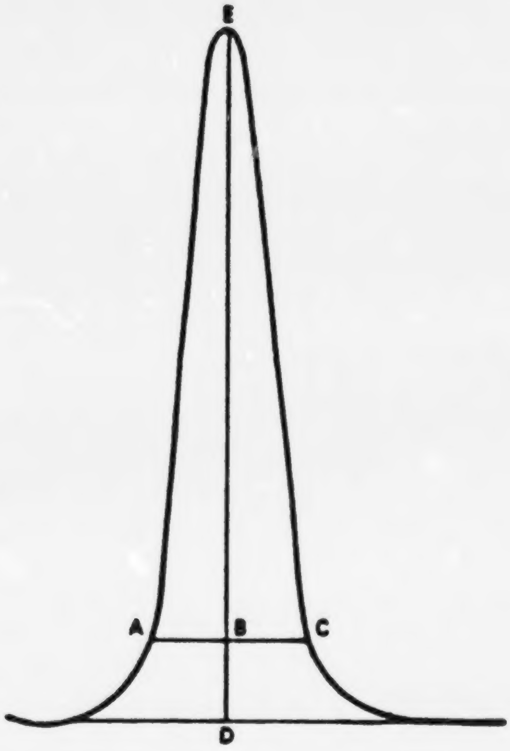


FIGURE 4. MASS SPECTROSCOPY SCAN (10 TO 150 AMV)
OF NDMA AT A RATE OF 0.5 TO 0.8 SCANS/SECOND

T07-20



Asymmetry Factor = $\frac{BC}{AB}$

Example Calculation:

Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm

Therefore: Asymmetry Factor = $\frac{12}{11}$ = 1.1

FIGURE 5. PEAK ASYMMETRY CALCULATION

TABLE 1: SUGGESTED PERFORMANCE CRITERIA FOR RELATIVE ION ABUNDANCES FROM FC-43 MASS CALIBRATION

M/E	% Relative Abundance
51	1.8 ± 0.5
69	100
100	12.0 ± 1.5
119	12.0 ± 1.5
131	35.0 ± 3.5
169	3.0 ± 0.4
219	24.0 ± 2.5
264	3.7 ± 0.4
314	0.25 ± 0.1

Revision 1.0
September, 1986

METHOD TO8 -1

METHOD FOR THE DETERMINATION OF PHENOL AND METHYLPHENOLS (CRESOLS) IN AMBIENT AIR USING HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

1. Scope

1.1 This document describes a method for determination of phenol and methylphenols (cresols) in ambient air. With careful attention to reagent purity and other factors, the method can detect these compounds at the 1-5 ppbv level.

1.2 The method as written has not been rigorously evaluated. The approach is a composite of several existing methods (1-3). The choice of HPLC detection system will be dependent on the requirements of the individual user. However, the UV detection procedure is considered to be most generally useful for relatively clean samples.

2. Applicable Documents

2.1 ASTM Standards
D1356 - Definitions of Terms Related to Atmospheric Sampling and Analysis(4).

2.2 Other Documents
U.S. EPA Technical Assistance Document (5).

3. Summary of Method

3.1 Ambient air is drawn through two midget impingers, each containing 15 mL of 0.1 N NaOH. The phenols are trapped as phenolates.

3.2 The impinger solutions are placed in a vial with a Teflon®-lined screw cap and returned to the laboratory for analysis. The solution is cooled in an ice bath and adjusted to pH <4 by addition of 1 mL of 5% v/v sulfuric acid. The sample is adjusted to a final volume of 25 mL with distilled water.

3.3 The phenols are determined using reverse-phase HPLC with either ultraviolet (UV) absorption detection at 274 nm, electrochemical detection, or fluorescence detection. In general, the UV detection approach should be used for relatively clean samples.

4. Significance

4.1 Phenols are emitted into the atmosphere from chemical operations and various combustion sources. Many of these compounds are acutely toxic, and their determination in ambient air is required in order to assess human health impacts.

4.2 Conventional methods for phenols have generally employed colorimetric or gas chromatographic techniques with relatively large detection limits. The method described here reduces the detection limit through use of HPLC.

5. Definitions

Definitions used in this document and in any user-prepared Standard Operating Procedures (SOPs) should be consistent with ASTM D1356 (5). All abbreviations and symbols are defined within this document at the point of use.

6. Interferences

6.1 Compounds having the same retention times as the compounds of interest will interfere in the method. Such interferences can often be overcome by altering the separation conditions (e.g., using alternative HPLC columns or mobile phase compositions) or detectors. Additionally, the phenolic compounds of interest in this method may be oxidized during sampling. Validation experiments may be required to show that the four target compounds are not substantially degraded.

6.2 If interferences are suspected in a "dirty" sample, preliminary cleanup steps may be required to identify interfering compounds by recording infrared spectrophotometry followed by specific ion-exchange column chromatography. Likewise, overlapping HPLC peaks may be resolved by increasing/decreasing component concentration of the mobile phase.

6.3 All reagents must be checked for contamination before use.

7. Apparatus

7.1 Isocratic HPLC system consisting of a mobile-phase reservoir, a high-pressure pump, an injection valve, a Zorbax ODS or C-18 reverse-phase column, or equivalent (25 cm x 4.6 mm ID), a variable-wavelength UV detector operating at 274 nm, and a data system or strip-chart recorder (Figure 1). Amperometric (electrochemical) or fluorescence detectors may also be employed.

7.2 Sampling system - capable of accurately and precisely sampling 100-1000 mL/minute of ambient air (Figure 2).

7.3 Stopwatch.

7.4 Friction-top metal can, e.g., one-gallon (paint can) - to hold samples.

7.5 Thermometer - to record ambient temperature.

7.6 Barometer (optional).

7.7 Analytical balance - 0.1 mg sensitivity.

7.8 Midget impingers - jet inlet type, 25-mL.

7.9 Suction filtration apparatus - for filtering HPLC mobile phase.

7.10 Volumetric flasks - 100 mL and 500 mL.

7.11 Pipettes - various sizes, 1-10 mL.

7.12 Helium purge line (optional) - for degassing HPLC mobile phase.

7.13 Erlenmeyer flask, 1 L - for preparing HPLC mobile phase.

7.14 Graduated cylinder, 1 L - for preparing HPLC mobile phase.

7.15 Microliter syringe, 100-250 uL - for HPLC injection.

8. Reagents and Materials

8.1 Bottles, 10 oz, glass, with Teflon®-lined screw cap - for storing sampling reagent.

8.2 Vials, 25 mL, with Teflon®-lined screw cap - for holding samples.

8.3 Disposable pipettes and bulbs.

8.4 Granular charcoal.

8.5 Methanol - distilled in glass or pesticide grade.

8.6 Sodium hydroxide - analytical reagent grade.

8.7 Sulfuric acid - analytical reagent grade.

8.8 Reagent water - purified by ion exchange and carbon filtration, or distillation.

8.9 Polyester filters, 0.22 um - Nuclepore, or equivalent.

8.10 Phenol, 2-methyl-, 3-methyl-, and 4-methylphenol - neat standards (99+ % purity) for instrument calibration.

8.11 Sampling reagent, 0.1 N NaOH. Dissolve 4.0 grams of NaOH in reagent water and dilute to a final volume of 1 L. Store in a glass bottle with Teflon®-lined cap.

8.12 Sulfuric acid, 5% v/v. Slowly add 5 mL of concentrated sulfuric acid to 95 mL of reagent water.

8.13 Acetate buffer, 0.1M, pH 4.8 - Dissolve 5.8 mL of glacial acetic acid and 13.6 grams of sodium acetate trihydrate in 1 L of reagent water.

8.14 Acetonitrile - spectroscopic grade.

8.15 Glacial acetic acid - analytical reagent grade.

8.16 Sodium acetate trihydrate - analytical reagent grade.

9. Sampling

9.1 The sampling apparatus is assembled and should be similar to that shown in Figure 2. EPA Federal Reference Method 6 uses essentially the same sampling system (6). All glassware (e.g., impingers, sampling bottles, etc.) must be thoroughly rinsed with methanol and oven-dried before use.

9.2 Before sample collection, the entire assembly (including empty sample impingers) is installed and the flow rate checked at a value near the desired rate. In general, flow rates of 100-1000 mL/minute are useful. Flow rates greater than 1000 mL/minute should not be used because impinger collection efficiency may decrease. Generally, calibration is accomplished using a soap bubble flow meter or calibrated wet test meter connected to the flow exit, assuming the entire system is sealed. ASTM Method D3686 describes an appropriate calibration scheme that does not require a sealed-flow system downstream of the pump (4).

9.3 Ideally, a dry gas meter is included in the system to record total flow, if the flow rate is sufficient for its use. If a dry gas meter is not available, the operator must measure and record the sampling flow rate at the beginning and end of the sampling period to determine sample volume. If the sampling time exceeds two hours, the flow rate should be measured at intermediate points during the sampling period. Ideally, a rotameter should be included to allow observation of the flow rate without interruption of the sampling process.

9.4 To collect an air sample, two clean midget impingers are loaded with 15 mL of 0.1 N NaOH each and sample flow is started. The following parameters are recorded on the data sheet (see Figure 3 for an example): date, sampling location, time, ambient temperature, barometric pressure (if available), relative humidity (if available), dry gas meter reading (if appropriate), flow rate, rotameter setting, 0.1 N NaOH reagent batch number, and dry gas meter and pump identification numbers.

9.5 The sampler is allowed to operate for the desired period, with periodic recording of the variables listed above. The total volume should not exceed 80 L. The operator must ensure that at least 5 mL of reagent remains in the impinger at the end of the sampling interval. (Note: for high ambient temperatures, lower sampling volumes may be required.)

9.6 At the end of the sampling period, the parameters listed in Section 9.4 are recorded and the sample flow is stopped. If a dry gas meter is not used, the flow rate must be checked at the end of the sampling interval. If the flow rates at the beginning and end of the sampling period differ by more than 15%, the sample should be discarded.

9.7 Immediately after sampling, the impinger is removed from the sampling system. The contents of the impinger are emptied into a clean 25-mL glass vial with a Teflon®-lined screw-cap. The impinger is then rinsed with 5 mL of reagent water and the rinse solution is added to the vial. The vial is then capped, sealed with Teflon® tape, and placed in a friction-top can containing 1-2 inches of granular charcoal. The samples are stored in the can and refrigerated until analysis. No degradation has been observed if the time between refrigration and analysis is less than 48 hours.

9.8 If a dry gas meter or equivalent total flow indicator is not used, the average sample flow rate must be calculated according to the following equation:

$$Q_A = \frac{Q_1 + Q_2 + \cdots Q_N}{N}$$

where

Q_A = average flow rate (mL/minute).

$Q_1, Q_2, \ldots . Q_N$ = flow rates determined at beginning, end, and intermediate points during sampling.

N = number of points averaged.

9.9 The total flow is then calculated using the following equation:

$$V_m = \frac{(T_2 - T_1) \times Q_A}{1000}$$

where

V_m = total volume (L) sampled at measured temperature and pressure.
T_2 = stop time.
T_1 = start time.
T_2-T_1 = total sampling time (minutes).
Q_A = average flow rate (ml/minute).

9.10 The volume of air sampled is often reported uncorrected for atmospheric conditions (i.e., under ambient conditions). However, the value should be adjusted to standard conditions (25°C and 760 mm pressure) using the following equation:

$$V_s = V_m \times \frac{P_A}{760} \times \frac{298}{273 + T_A}$$

where

V_s = total sample volume (L) at 25°C and 760 mm Hg pressure.
V_m = total sample volume (L) under ambient conditions. Calculated as in Section 9.9 or from dry gas meter reading.
P_A = ambient pressure (mm Hg).
T_A = ambient temperature (°C).

10. Sample Analysis

10.1 Sample Preparation

10.1.1 The samples are returned to the laboratory in 25-mL screw-capped vials. The contents of each vial are transferred to a 25-mL volumetric flask. A 1-mL volume of 5% sulfuric acid is added and the final volume is adjusted to 25 mL with reagent water.

10.1.2 The solution is thoroughly mixed and then placed in a 25-ml screw-capped vial for storage (refrigerated) until HPLC analysis.

10.2 HPLC Analysis

10.2.1 The HPLC system is assembled and calibrated as described in Section 11. The operating parameters are as follows:

Column: C-18 RP
Mobile Phase: 30% acetonitrile/70% acetate buffer solution
Detector: ultraviolet, operating at 274 nm
Flow Rate: 0.3 mL/minute
Retention Time:

Individual
phenol - 9.4 minutes
o-cresol - 12.5 minutes
m-cresol - 11.5 minutes
p-cresol - 11.9 minutes

Combined
phenol - 9.4 minutes
o-cresol - 12.8 minutes
m/p-cresol - 11.9 minutes

Before each analysis, the detector baseline is checked to ensure stable operation.

10.2.2 A 100-uL aliquot of the sample is drawn into a clean HPLC injection syringe. The sample injection loop (50 uL) is loaded and an injection is made. The data system, if available, is activated simultaneously with the injection and the point of injection is marked on the strip-chart recorder.

10.2.3 After approximately one minute, the injection valve is returned to the "load" position and the syringe and valve are flushed with water in preparation for the next sample analysis.

10.2.4 After elution of the last component of interest, data acquisition is terminated and the component concentrations are calculated as described in Section 12.

10.2.5 Phenols have been successfully separated from cresols utilizing HPLC with the above operating parameters. However, meta- and para-cresols have not been successfully separated. Figure 4 illustrates a typical chromatogram.

10.2.6 After a stable baseline is achieved, the system can be used for further sample analyses as described above.

10.2.7 If the concentration of analyte exceeds the linear range of the instrument, the sample should be diluted with mobile phase, or a smaller volume can be injected into the HPLC.

10.2.8 If the retention time is not duplicated, as determined by the calibration curve, you may increase or decrease the acetonitrile/water ratio to obtain the correct elution time, as specified in Figure 4. If the elution time is long, increase the ratio; if it is too short, decrease the ratio.

11.0 HPLC Assembly and Calibration

11.1 The HPLC system is assembled and operated according to Section 10.2.1.

11.2 The HPLC mobile phase is prepared by mixing 300 mL of acetonitrile and 750 mL of acetate buffer, pH 4.8. This mixture is filtered through a 0.22-um polyester membrane filter in an all-glass and Teflon® suction filtration apparatus. The filtered mobile phase is degassed by purging with helium for 10-15 minutes (100 mL/minute) or by heating to 60°C for 5-10 minutes in an Erlenmeyer flask covered with a watch glass. A constant back pressure restrictor (50 psi) or short length (6-12 inches) of 0.01-inch I.D. Teflon® tubing should be placed after the detector to eliminate further mobile phase outgassing.

11.3 The mobile phase is placed in the HPLC solvent reservoir and the pump is set at a flow rate of 0.3 mL/minute and allowed to pump for 20-30 minutes before the first analysis. The detector is switched on at least 30 minutes before the first analysis and the detector output is displayed on a strip-chart recorder or similar output device. UV detection at 274 nm is generally preferred. Alternatively, fluorescence detection with 274-nm excitation at 298-nm emission (2), or electrochemical detection at 0.9 volts (glassy carbon electrode versus Ag/AgCl) (3) may be used. Once a stable baseline is achieved, the system is ready for calibration.

11.4 Calibration standards are prepared in HPLC mobile phase from the neat materials. Individual stock solutions of 100 mg/L are prepared by dissolving 10 mg of solid derivative in 100 mL of mobile phase. These individual solutions are used to prepare calibration standards containing all of the phenols and cresols of interest at concentrations spanning the range of interest.

11.5 Each calibration standard (at least five levels) is analyzed three times and area response is tabulated against mass injected. Figures 5a through 5e illustrate HPLC response to various phenol concentrations (1 mL/minute flow rate). All calibration runs are performed as described for sample analyses in Section 10. Using the UV detector, a linear response range of approximately 0.05 to 10 mg/L should be achieved for 50-uL injection volumes. The results may be used to prepare a calibration curve, as illustrated in Figure 6 for phenols. Linear response is indicated where a correlation coefficient of at least 0.999 for a linear least-squares fit of the data (concentration versus area response) is obtained. The retention times for each analyte should agree within 2%.

11.6 Once linear response has been documented, an intermediate concentration standard near the anticipated levels for each component, but at least 10 times the detection limit, should be chosen for daily calibration. The response for the various components should be within 10% day to day. If greater variability is observed, recalibration may be required or a new calibration curve must be developed from fresh standards.

11.7 The response for each component in the daily calibration standard is used to calculate a response factor according to the following equation:

$$RF_c = \frac{C_c \times V_I}{R_c}$$

where

RF_c = response factor (usually area counts) for the component of interest in nanograms injected/response unit.

C_c = concentration (mg/L) of analyte in the daily calibration standard.

V_I = volume (uL) of calibration standard injected.

R_c = response (area counts) for analyte in the calibration standard.

12. Calculations

12.1 The concentration of each compound is calculated for each sample using the following equation:

$$W_d = RF_c \times R_d \times \frac{V_E}{V_I} \times \frac{V_D}{V_A}$$

where

W_d = total quantity of analyte (ug) in the sample.

RF_c = response factor calculated in Section 11.6.

R_d = response (area counts or other response units) for analyte in sample extract.

V_E = final volume (mL) of sample extract.

V_I = volume of extract (uL) injected onto the HPLC system.

V_D = redilution volume (if sample was rediluted).

V_A = aliquot used for redilution (if sample was rediluted).

12.2 The concentration of analyte in the original sample is calculated from the following equation:

$$C_A = \frac{W_d}{V_m \text{ (or } V_s\text{)}} \times 1000$$

where

C_A = concentration of analyte (ng/L) in the original sample.
W_d = total quantity of analyte (ug) in sample.
V_m = total sample volume (L) under ambient conditions.
V_s = total sample volume (L) at 25 °C and 760 mm Hg.

12.3 The analyte concentrations can be converted to ppbv using the following equation:

$$C_A \text{ (ppbv)} = C_A \text{ (ng/L)} \times \frac{24.4}{MW_A}$$

where

C_A (ng/L) is calculated using V_s.
MW_A = molecular weight of analyte.

13. Performance Criteria and Quality Assurance

This section summarizes required quality assurance (QA) measures and provides guidance concerning performance criteria that should be achieved within each laboratory.

13.1 Standard Operating Procedures (SOPs).

13.1.1 Users should generate SOPs describing the following activities in their laboratory: (1) assembly, calibration, and operation of the sampling system, with make and model of equipment used; (2) preparation, purification, storage, and handling of sampling reagent and samples; (3) assembly, calibration, and operation of the HPLC system, with make and model of equipment used; and (4) all aspects of data recording and processing, including lists of computer hardware and software used.

13.1.2 SOPs should provide specific stepwise instructions and should be readily available to and understood by the laboratory personnel conducting the work.

13.2 HPLC System Performance

13.2.1 The general appearance of the HPLC chromatogram should be similar to that illustrated in Figure 4.

13.2.2 The HPLC system efficiency and peak asymmetry factor should be determined in the following manner: A solution of phenol corresponding to at least 20 times the detection limit should be injected with the recorder chart sensitivity and speed set to yield a peak approximately 75% of full scale and 1 cm wide at half height. The peak asymmetry factor is determined as shown in Figure 7, and should be betweeen 0.8 and 1.8.

13.2.3 HPLC system efficiency is calculated according to the following equation:

$$N = 5.54 \left(\frac{t_r}{W_{1/2}} \right)^2$$

where

N = column efficiency (theoretical plates).
t_r = retention time (seconds) of analyte.
$W_{1/2}$ = width of component peak at half height (seconds).

A column efficiency of >5,000 theoretical plates should be obtained.

13.2.4 Precision of response for replicate HPLC injections should be ±10% or less, day to day, for calibration standards. Precision of retention times should be ±2%, on a given day.

13.3 Process Blanks

13.3.1 Before use, a 15-mL aliquot of each batch of 0.1 N NaOH reagent should be analyzed as described in Section 10. In general, analyte levels equivalent to <5 ng/L in an 80-L sample should be achieved.

13.3.2 At least one field blank, or 10% of the field samples, whichever is larger, should be shipped and analyzed with each group of samples. The number of samples within a group and/or time frame should be recorded so that a specified percentage of blanks is obtained for a given number of field samples. The field blank is treated identically to the samples except that no air is drawn through the reagent. The same performance criteria described in Section 13.3.1 should be met for process blanks.

13.4 Method Precision and Accuracy

13.4.1 At least one duplicate sample, or 10% of the field samples, whichever is larger, should be collected during each sampling episode. Precision for field replication should be ±20% or better.

13.4.2 Precision for replicate HPLC injections should be ±10% or better, day to day, for calibration standards.

13.4.3 At least one spiked sample, or 10% of the field samples, whichever is larger, should be collected. The impinger solution is spiked with a known quantity of the compound of interest, prepared as a dilute water solution. A recovery of >80% should be achieved routinely.

13.4.4 Before initial use of the method, each laboratory should generate triplicate spiked samples at a minimum of three concentration levels, bracketing the range of interest for each compound. Triplicate nonspiked samples must also be processed. Spike recoveries of >80 ±10% and blank levels of <5 ng/L (using an 80-L sampling volume) should be achieved.

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(5) Riggin, R. M., "Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air," EPA-600/4-83-027, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1983.

(6) "Method 6 Determination of SO_2 Emissions from Stationary Sources," Federal Register, Vol. 42., No. 160, August, 1977.

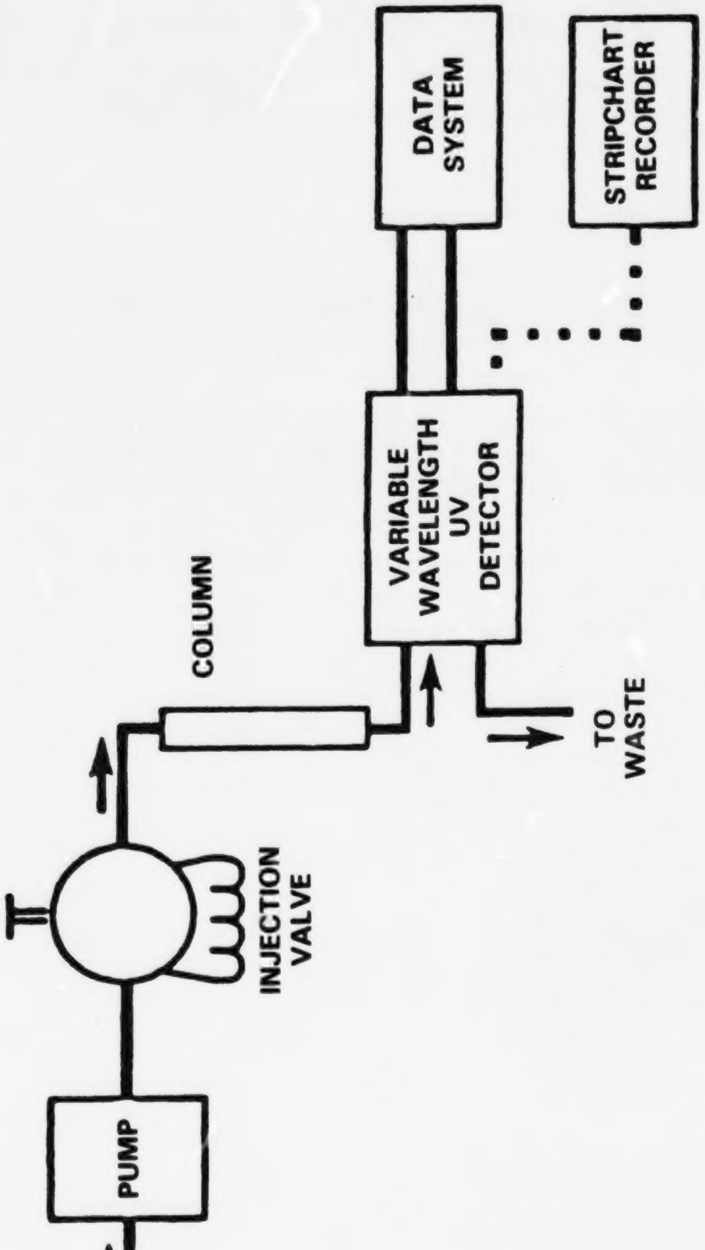

MOBILE
PHASE
RESERVOIR
PUMP
INJECTION
VALVE
COLUMN
VARIABLE
WAVELENGTH
UV
DETECTOR
TO
WASTE
DATA
SYSTEM
STRIPCHART
RECORDER

FIGURE 1. TYPICAL HPLC SYSTEM

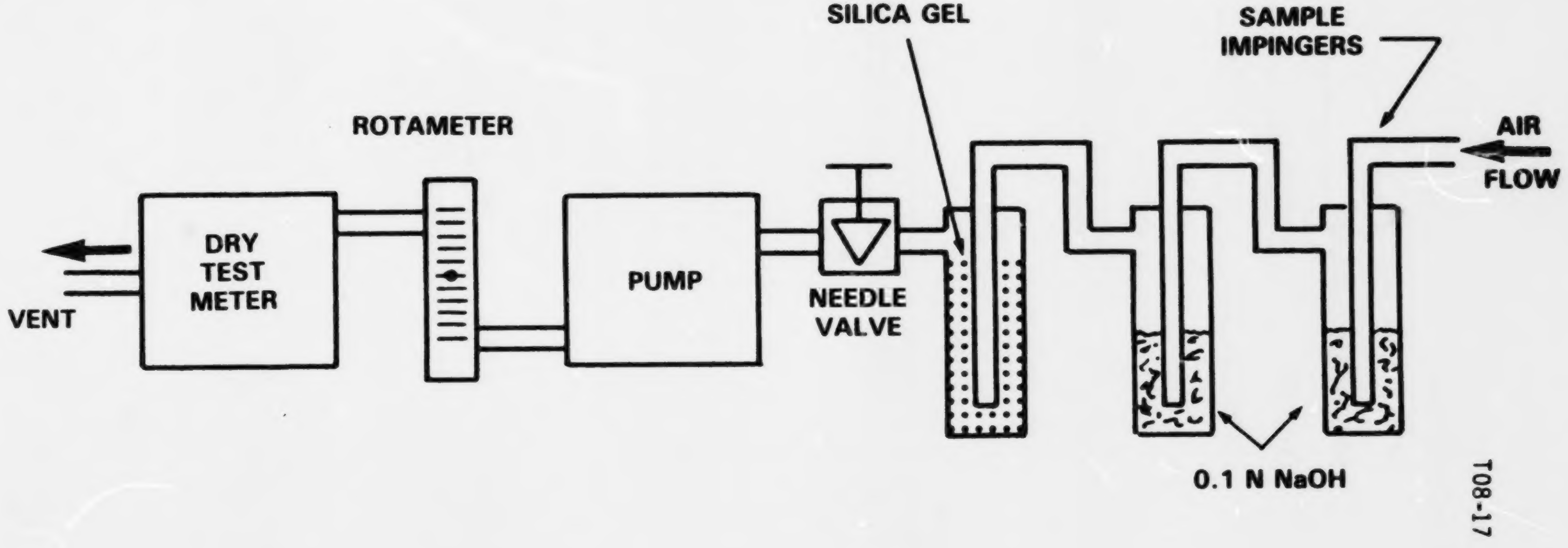

SILICA GEL
SAMPLE IMPINGERS
ROTAMETER
AIR FLOW
DRY TEST METER
PUMP
NEEDLE VALVE
VENT
0.1 N NaOH
T08-17

FIGURE 2. TYPICAL SAMPLING SYSTEM FOR MONITORING PHENOLS/CRESOLS IN AMBIENT AIR

SAMPLING DATA SHEET
(One Sample per Data Sheet)

PROJECT: ____________________

SITE: ____________________

LOCATION: ____________________

INSTRUMENT MODEL NO: ____________

PUMP SERIAL NO: ____________

DATES(S) SAMPLED: ____________

TIME PERIOD SAMPLED: ____________

OPERATOR: ____________

CALIBRATED BY: ____________

SAMPLING DATA

Sample Number: ____________

Start Time: __________ Stop Time: __________

Time	Dry Gas Meter Reading	Rotameter Reading	Flow Rate,*Q mL/min	Ambient Temperature °C	Barometric Pressure, mm Hg	Relative Humidity, %	Comments
1.							
2.							
3.							
4.							
N.							

Total Volume Data**

V_m = (Final - Initial) Dry Gas Meter Reading, or = ______ L

$$= \frac{Q_1 + Q_2 + Q_3 \cdots Q_N}{N} \times \frac{1}{1000 \times (\text{Sampling Time in Minutes})} = \_\_\_\_\_\_ \text{ L}$$

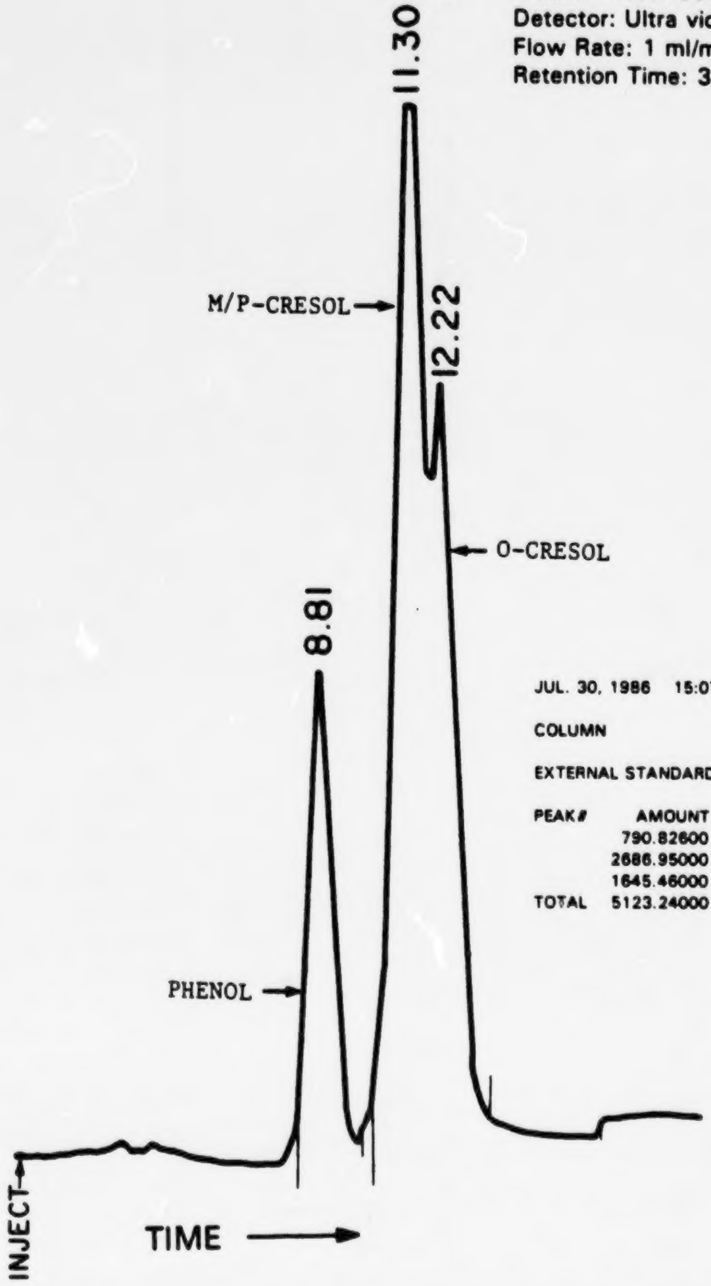
* Flow rate from rotameter or soap bubble calibrator (specify which).

** Use data from dry gas meter if available.

FIGURE 3. EXAMPLE SAMPLING DATA SHEET

OPERATING PARAMETERS
HPLC

Column: C-18 RP
Mobile Phase: 30% Acetonitrile/70% Acetate Buffer
Detector: Ultra violet operating at 274 nm
Flow Rate: 1 ml/min
Retention Time: 3.4 minutes

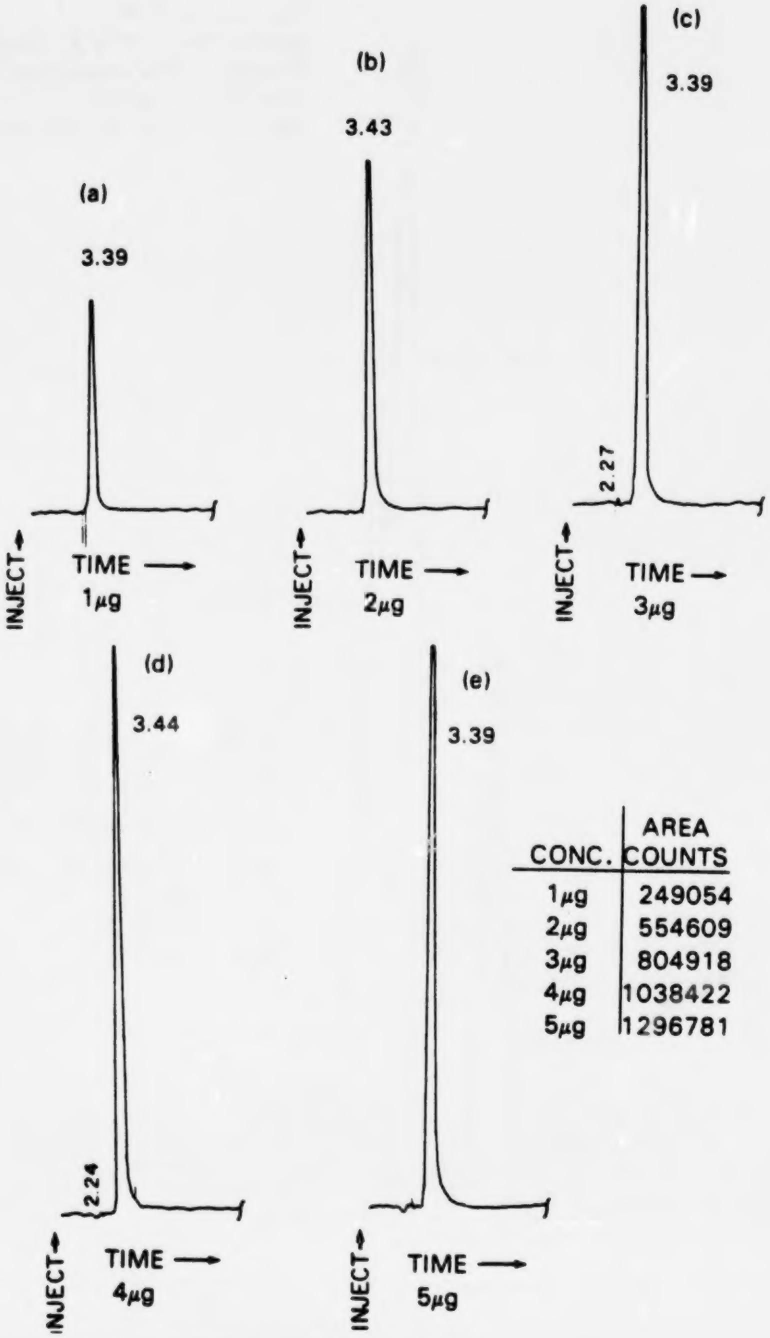


```
JUL. 30, 1986   15:07:17   CHART 0.50 CM/MIN
                           RUN #43    CALC #0
COLUMN                     SOLVENT   OPR ID:         3

EXTERNAL STANDARD QUANTITATION

PEAK#      AMOUNT    RT     EXP RT         AREA           RF
         790.82600    8.81               790826 L   0.000000E0
        2686.95000   11.30              2686966 F   0.000000E0
        1645.46000   12.22              1645466 L   0.000000E0
TOTAL   5123.24000
```

FIGURE 4. TYPICAL CHROMATOGRAM ILLUSTRATING SEPARATION OF PHENOLS/CRESOLS BY HPLC



CONC.	AREA COUNTS
1μg	249054
2μg	554609
3μg	804918
4μg	1038422
5μg	1296781

FIGURE 5a-5e. HPLC CHROMATOGRAM OF VARYING PHENOL CONCENTRATIONS

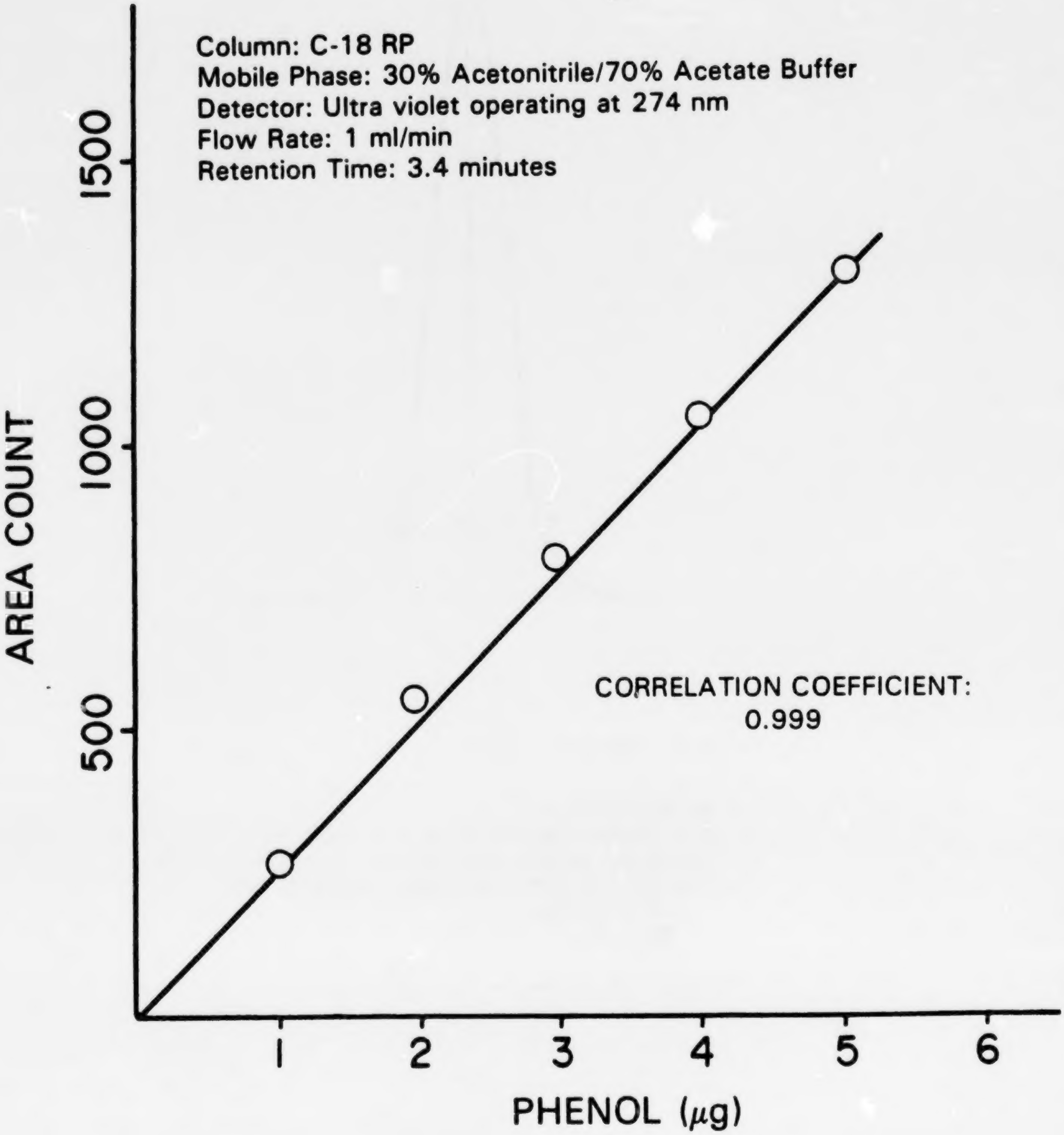
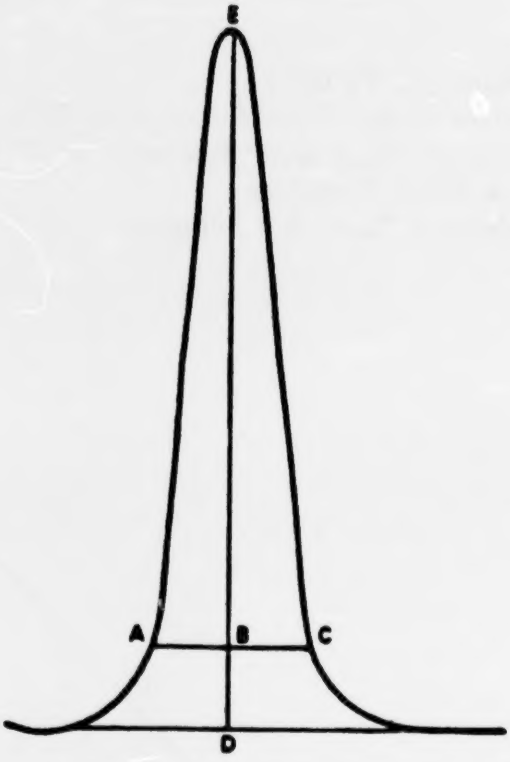


FIGURE 6. CALIBRATION CURVE FOR PHENOL



Asymmetry Factor = $\frac{BC}{AB}$

Example Calculation:

Peak Height = DE = 100 mm

10% Peak Height = BD = 10 mm

Peak Width at 10% Peak Height = AC = 23 mm

AB = 11 mm

BC = 12 mm

Therefore: Asymmetry Factor = $\frac{12}{11}$ = 1.1

FIGURE 7. PEAK ASYMMETRY CALCULATION

Revision 1.1
June, 1988

METHOD T09 - 1

METHOD FOR THE DETERMINATION OF POLYCHLORINATED DIBENZO-p-DIOXINS (PCDDs) IN AMBIENT AIR USING HIGH-RESOLUTION GAS CHROMATOGRAPHY/HIGH-RESOLUTION MASS SPECTROMETRY (HRGC/HRMS)

1. Scope

1.1 This document describes a method for the determination of polychlorinated dibenzo-p-dioxins (PCDDs) in ambient air. In particular, the following PCDDs have been evaluated in the laboratory utilizing this method:

- 1,2,3,4-tetrachlorodibenzo-p-dioxin (1,2,3,4-TCDD)
- 1,2,3,4,7,8-hexachlorodibenzo-p-dioxin (1,2,3,4,7,8-H_xCDD)
- Octachlorodibenzo-p-dioxin (OCDD)
- 2,3,7,8-Tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD)

The method consists of sampling ambient air via an inlet filter followed by a cartridge (filled with polyurethane foam) and analysis of the sample using high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS). Original laboratory studies have indicated that the use of polyurethane foam (PUF) or silica gel in the sampler will give equal efficiencies for retaining PCDD/PCDF isomers; i.e., the median retention efficiencies for the PCDD isomers ranged from 67 to 124 percent with PUF and from 47 to 133 percent with silica gel. Silica gel, however, produced lower levels of background interferences than PUF. The detection limits were, therefore, approximately four times lower for tetrachlorinated isomers and ten times lower for hexachlorinated isomers when using silica gel as the adsorbent. The difference in detection limit was approximately a factor of two for the octachlorinated isomers. However, due to variable recovery and extensive cleanup required with silica gel, the method has been written using PUF as the adsorbent.

1.2 With careful attention to reagent purity and other factors, the method can detect PCDDs in filtered air at levels below 1-5 pg/m^3*.

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*Lowest levels for which the method has been validated. Up to an order of magnitude better sensitivity should be achievable with 24-hour air samples.

1.3 Average recoveries ranged from 68 percent to 140 percent in laboratory evaluations of the method sampling ultrapure filtered air. Percentage recoveries and sensitivities obtainable for ambient air samples have not been determined.

2. Applicable Documents

2.1 ASTM Standards

2.1.1 Method D1356 - Definitions of Terms Relating to Atmospheric Sampling and Analysis.

2.1.2 Method E260 - Recommended Practice for General Gas Chromatography Procedures.

2.1.3 Method E355 - Practice for Gas Chromatography Terms and Relationships.

2.2 EPA Documents

2.2.1 Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II - "Ambient Air Specific Methods," Section 2.2 - "Reference Method for the Determination of Suspended Particulates in the Atmosphere," Revision 1, July, 1979, EPA-600/4-77-027A.

2.2.2. Protocol for the Analysis of 2,3,7,8-Tetrachlorodibenzo-p-Dioxin by High Resolution Gas Chromatography-High Resolution Mass Spectrometry, U.S. Environmental Protection Agency, January, 1986, EPA-600/4-86-004.

2.2.3 Evaluation of an EPA High Volume Air Sampler for Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans, undated report by Battelle under Contract 68-02-4127, Project Officers Robert G. Lewis and Nancy K. Wilson, U.S. Environmental Protection Agency, EMSL, Research Triangle Park, North Carolina.

2.2.4 Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, U.S. Environmental Protection Agency, April, 1984, 600/4-84-041.

2.2.5 Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air, U.S. Environmental Protection Agency, June, 1983, EPA-600/4-83-027.

2.3 Other Documents

2.3.1 General Metal Works Operating Procedures for Model PS-1 Sampler, General Metal Works, Inc., Village of Cleves, Ohio.

2.3.2 Chicago Air Quality: PCB Air Monitoring Plan, Phase 2, Illinois Environmental Protection Agency, Division of Air Pollution Control, April, 1986, IEPA/APC/86-011.

3. Summary of Method

3.1 Filters and adsorbent cartridges (containing PUF) are cleaned in solvents and vacuum-dried. The filters and adsorbent cartridges are stored in screw-capped jars wrapped in aluminum foil (or otherwise protected from light) before careful installation on a modified high volume sampler.

3.2 Approximately 325 m^3 of ambient air is drawn through a cartridge on a calibrated General Metal Works Model PS-1 Sampler, or equivalent (breakthrough has not been shown to be a problem with sampling volumes of 325 m^3).

3.3 The amount of air sampled through the adsorbent cartridge is recorded, and the cartridge is placed in an appropriately labeled container and shipped along with blank adsorbent cartridges to the analytical laboratory for analysis.

3.4 The filters and PUF adsorbent cartridge are extracted together with benzene. The extract is concentrated, diluted with hexane, and cleaned up using column chromatography.

3.5 The High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS) system is verified to be operating properly and is calibrated with five concentration calibration solutions, each analyzed in triplicate.

3.6 A preliminary analysis of a sample of the extract is performed to check the system performance and to ensure that the samples are within the calibration range of the instrument. If necessary, recalibrate the instrument, adjust the amount of the sample injected, adjust the calibration solution concentration, and adjust the data processing system to reflect observed retention times, etc.

3.7 The samples and the blanks are analyzed by HRGC/HRMS and the results are used (along with the amount of air sampled) to calculate the concentrations of polychlorinated dioxins in ambient air.

4. Significance

4.1 Polychlorinated dibenzo-p-dioxins (PCDDs) are extremely toxic. They are carcinogenic and are of major environmental concern. Certain isomers, for example, 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), have LD50 values in the parts-per-trillion range for some animal species. Major sources of these compounds have been commercial processes involving polychlorinated phenols and polychlorinated biphenyls (PCBs). Recently, however, combustion sources have been shown to emit polychlorinated dibenzo-p-dioxin (PCDD), including the open-flame combustion of wood containing chlorophenol wood preservatives, and emissions from burning transformers and/or capacitors that contain PCBs and chlorobenzenes.

4.2 Several documents have been published which describe sampling and analytical approaches for PCDDs, as outlined in Section 2.2. The attractive features of these methods have been combined in this procedure. This method has not been validated in its final form, and, therefore, one must use caution when employing it for specific applications.

4.3 The relatively low level of PCDDs in the environment requires the use of high volume sampling techniques to acquire sufficient samples for analysis. However, the volatility of PCDDs prevents efficient collection on filter media. Consequently, this method utilizes both a filter and a PUF backup cartridge which provides for efficient collection of most PCDDs.

5. Definitions

Definitions used in this document and in any user-prepared standard operating procedures (SOPs) should be consistent with ASTM Methods D1356 and E355 (Sections 2.1.1 and 2.1.3). All abbreviations and symbols within this document are defined the first time they are used.

6. Interferences

6.1 Chemicals that elute from the gas chromatographic (GC) column within ±10 scans of the standards or compounds of interest and which produce, within the retention time windows, ions with any mass-to-charge (m/e) ratios close enough to those of the ion fragments used to detect or quantify the analyte compounds are potential interferences. Most frequently encountered potential interferences are other sample components that are extracted along with PCDDs, e.g., polychlorinated biphenyls (PCBs), methoxybiphenyls, chlorinated hydroxydiphenylethers, chlorinated naphthalenes, DDE, DDT, etc. The actual incidence of interference by these compounds also depends upon relative concentrations, mass spectrometric resolution, and chromatographic conditions. Because very low levels of PCDDs must be measured, the elimination of interferences is essential. High-purity reagents and solvents must be used and all equipment must be scrupulously cleaned. Laboratory reagent blanks must be analyzed to demonstrate absence of contamination that would interfere with the measurements. Column chromatographic procedures are used to remove some coextracted sample components; these procedures must be performed carefully to minimize loss of analyte compounds during attempts to increase their concentration relative to other sample components.

6.2 In addition to chemical interferences, inaccurate measurements could occur if PCDDs are retained on particulate matter, the filter, or PUF adsorbent cartridge, or are chemically changed during sampling and storage in ways that are not accurately measured by adding isotopically labeled spikes to the samples.

6.3 The system cannot separately quantify gaseous PCDDs and particulate PCDDs because the material may be lost from the filter by volatilization after collection and may be transferred to the absorbent cartridge. Gaseous PCDDs may also be adsorbed on particulate matter on the filter.

7. Apparatus

7.1 General Metal Works (GMW) Model PS-1 Sampler.

7.2 At least two Model PS-1 sample cartridges and filters per PS-1 Sampler.

7.3 Calibrated GMW Model 40 calibrator.

7.4 High-Resolution Gas Chromatograph/High-Resolution Mass Spectrometer/Data System (HRGC/HRMS/DS)

7.4.1 The GC must be equipped for temperature programming, and all required accessories must be available, including syringes, gases, and a capillary column. The GC injection port must be designed for capillary columns. The use of splitless injection techniques is recommended. On-column injection techniques can be used but they may severely reduce column lifetime for nonchemically bonded columns. In this protocol, a 2-uL injection volume is used consistently. With some GC injection ports, however, 1-uL injections may produce some improvement in precision and chromatographic separation. A 1-uL injection volume may be used if adequate sensitivity and precision can be achieved.

[NOTE: If 1 uL is used as the injection volume, the injection volumes for all extracts, blanks, calibration solutions and performance check samples must be 1 uL.]

7.4.2 Gas Chromatograph-Mass Spectrometer Interface. The gas chromatograph is usually coupled directly to the mass spectrometer source. The interface may include a diverter valve for shunting the column effluent and isolating the mass spectrometer source. All components of the interface should be glass or glass-lined stainless steel. The interface components should be compatible with 300°C temperatures. Cold spots and/or active surfaces (adsorption sites) in the GC/MS interface can cause peak tailing and peak broadening. It is recommended that the GC column be fitted directly into the MS source. Graphic ferrules should be avoided in the GC injection area since they may adsorb TCDD. Vespel® or equivalent ferrules are recommended.

7.4.3 Mass Spectrometer. The static resolution of the instrument must be maintained at a minimum of 10,000 (10 percent valley). The mass spectrometer must be operated in a selected ion monitoring (SIM) mode with a total cycle time (including voltage reset time) of one second or less (Section 12.3.4.1). At a minimum, ions that occur at the following masses must be monitored:

2,3,7,8-TCDD	1,2,3,4,7,8-H_xCDD	OCDD
258.9300	326.8521	394.7742
319.8965	389.8156	457.7377
321.8936	391.8127	459.7347
331.9368		
333.93338		

7.4.4 Data System. A dedicated computer data system is employed to control the rapid multiple ion monitoring process and to acquire the data. Quantification data (peak areas or peak heights) and SIM traces (displays of intensities of each m/z being monitored as a function of time) must be acquired during the analyses. Quantifications may be reported based upon computer-generated peak areas or upon measured peak heights (chart recording). The detector zero setting must allow peak-to-peak measurement of the noise on the baseline.

7.4.5 GC Column. A fused silica column (30 m x 0.25 mm I.D.) coated with DB-5, 0.25 u film thickness (J & S Scientific, Inc., Crystal Lake, IL) is utilized to separate each of the several tetra- through octa-PCDDs, as a group, from all of the other groups. This column also resolves 2,3,7,8-TCDD from all 21 other TCDD isomers; therefore, 2,3,7,8-TCDD can be determined quantitatively if proper calibration procedures are followed as per Sections 12.3 through 12.6. Other columns may be used for determination of PCDDs, but separation of the wrong PCDD isomers must be demonstrated and documented. Minimum acceptance criteria must be determined as per Section 12.1. At the beginning of each 12-hour period (after mass resolution has been demonstrated) during which sample extracts or concentration calibration solutions will be analyzed, column operating conditions must be attained for the required separation on the column to be used for samples.

7.5 All required syringes, gases, and other pertinent supplies to operate the HRGC/HRMS system.

7.6 Airtight, labeled screw-capped containers to hold the sample cartridges (perferably glass with Teflon seals or other noncontaminating seals).

7.7 Data sheets for each sample for recording the location and sample time, duration of sample, starting time, and volume of air sampled.

7.8 Balance capable of weighing accurately to ±0.001 g.

7.9 Pipettes, micropipets, syringes, burets, etc., to make calibration and spiking solutions, dilute samples if necessary, etc., including syringes for accurately measuring volumes such as 25 uL and 100 uL of isotopically labeled dioxin solutions.

7.10 Soxhlet extractors capable of extracting GMW PS-1 PUF adsorbent cartridges (2.3" x 5" length), 500-mL flask, and condenser.

7.11 Vacuum drying oven system capable of maintaining the PUF cartridges being evacuated at 240 torr (flushed with nitrogen) overnight.

7.12 Ice chest - to store samples at 0°C after collection.

7.13 Glove box for working with extremely toxic standards and reagents with explosion-proof hood for venting fumes from solvents reagents, etc.

7.14 Adsorbtion columns for column chromatography - 1 cm x 10 cm and 1 cm x 30 cm, with stands.

7.15 Concentrator tubes and a nitrogen evaporation apparatus with variable flow rate.

7.16 Laboratory refrigerator with chambers operating at 0°C and 4°C.

7.17 Kuderna-Danish apparatus - 500 mL evaporating flask, 10 mL graduated concentrator tubes with ground-glass stoppers, and 3-ball macro Snyder Column (Kontes K-570001-0500, K-50300-0121, and K-569001-219, or equivalent).

7.18 Two-ball micro Snyder Column, Kuderna-Danish (Kontes 569001-0219, or equivalent).

7.19 Stainless steel spatulas and spoons.

7.20 Minivials - 1 mL, borosilicate glass, with conical reservoir and screw caps lined with Teflon-faced silicone disks, and a vial holder.

7.21 Chromatographic columns for Carbopak cleanup - disposable 5-mL graduated glass pipets, 6 to 7 mm ID.

7.22 Desiccator.

7.23 Polyester gloves for handling PUF cartridges and filter.

7.24 Die - to cut PUF plugs.

7.25 Water bath equipped with concentric ring cover and capable of being temperature-controlled within ±2°C.

7.26 Erlenmeyer flask, 50 mL.

7.27 Glass vial, 40 mL.

7.28 Cover glass petri dishes for shipping filters.

7.29 Fritted glass extraction thimbles.

7.30 Pyrex glass tube furnace system for activating silica gel at 180°C under purified nitrogen gas purge for an hour, with capability of raising temperature gradually.

[NOTE: Reuse of glassware should be minimized to avoid the risk of cross-contamination. All glassware that is used, especially glassware that is reused, must be scrupulously cleaned as soon as possible after use. Rinse glassware with the last solvent used in it and then with high-purity acetone and hexane. Wash with hot water containing detergent. Rinse with copious amount of tap water and several portions of distilled water. Drain, dry, and heat in a muffle furnace at 400°C for 2 to 4 hours. Volumetric glassware must not be heated in a muffle furnace; rather, it should be rinsed with high-purity acetone and hexane. After the glassware is dry and cool, rinse it with hexane, and store it inverted or capped with solvent-rinsed aluminum foil in a clean environment.]

8. Reagents and Materials

8.1 Ultrapure glass wool, silanized, extracted with methylene chloride and hexane, and dried.

8.2 Ultrapure acid-washed quartz fiber filters for PS-1 Sampler (Pallfex 2500 glass, or equivalent).

8.3 Benzene (Burdick and Jackson, glass-distilled, or equivalent).

8.4 Hexane (Burdick and Jackson, glass-distilled, or equivalent).

8.5 Alumina, acidic - extracted in a Soxhlet apparatus with methylene chloride for 6 hours (minimum of 3 cycles per hour) and activated by heating in a foil-covered glass container for 24 hours at 190°C.

8.6 Silica gel - high-purity grade, type 60, 70-230 mesh; extracted in a Soxhlet apparatus with methylene chloride for 6 hours (minimum of 3 cycles per hour) and activated by heating in a foil-covered glass container for 24 hours at 130°C.

8.7 Silica gel impregnated with 40 percent (by weight) sulfuric acid - prepared by adding two parts (by weight) concentrated sulfuric acid to three parts (by weight) silica gel (extracted and activated) and mixiing with a glass rod until free of lumps; stored in a screw-capped glass bottle.

8.8 Graphitized carbon black (Carbopak C or equivalent), surface of approximately 12 m^2/g, 80/100 mesh - prepared by thoroughly mixing 3.6 grams Carbopak C and 16.4 grams Celite 545® in a 40-mL vial and activating at 130°C for six hours; stored in a desiccator.

8.9 Sulfuric Acid, ultrapure, ACS grade, specific gravity 1.84.

8.10 Sodium Hydroxide, ultrapure, ACS grade.

8.11 Native and isotopically labeled PCDD/PCDF isomers for calibration and spiking standards, from Cambridge Isotopes, Cambridge, MA.

8.12 n-decane (Aldrich Gold Label grade [D90-1], or equivalent).

8.13 Toluene (high purity, glass-distilled).

8.14 Acetone (high purity, glass-distilled).

8.15 Filters, quartz fiber - Pallflex 2500 QAST, or equivalent.

8.16 Ultrapure nitrogen gas (Scott chromatographic grade, or equivalent).

8.17 Methanol (chromatographic grade).

8.18 Methylene chloride (chromatographic grade, glass-distilled).

8.19 Dichloromethane/hexane (3:97, v/v), chromatographic grade.

8.20 Hexane/dichloromethane (1:1, v/v), chromatogtraphic grade.

8.21 Perfluorokerosene (PFK), chromatographic grade.

8.22 Celite 545®, reagent grade, or equivalent.

8.23 Membrane filters or filter paper with pore sizes less than 25 um, hexane-rinsed.

8.24 Granular anhydrous sodium sulfate, reagent grade.

8.25 Potassium carbonate-anhydrous, granular, reagent grade.

8.26 Cyclohexane, glass-distilled.

8.27 Tridecane, glass-distilled.

8.28 2,2,3-trimethylpentane, glass-distilled.

8.29 Isooctane, glass-distilled.

8.30 Sodium sulfate, ultrapure, ACS grade.

8.31 Polyurethane foam - 3 inches thick sheet stock, polyether type used in furniture upholstering, density 0.022 g/cm^3.

8.32 Concentration calibration solutions (Table 1) - four tridecane solutions containing $^{13}C_{12}$-1,2,3,4-TCDD (recovery standard) and unlabeled 2,3,7,8-TCDD at varying concentrations, and $^{13}C_{12}$-2,3,7,8-TCDD (internal standard, CAS RN 80494-19-5). These solutions must be obtained from the Quality Assurance Division, U.S. EPA, Environmental Monitoring Systems Laboratory (EMSL-LV), Las Vegas, Nevada, and must be used to calibrate the instrument. However, secondary standards may be obtained from commercial sources, and solutions may be prepared in the analytical laboratory. Traceability of standards must be verified against EPA-supplied standard solutions by procedures documented in laboratory SOPs. Care must be taken to use the correct standard. Serious overloading of instruments may occur if concentration calibration solutions intended for low-resolution MS are injected into the high-resolution MS.

8.33 Column performance check mixture dissolved in 1 mL of tridecane from Quality Assurance Division (EMSL-LV). Each ampule of this solution will contain approximately 10 ng of the following components (A) eluting near 2,3,7,8-TCDD and of the first (F) and last-eluting (L) TCDDs, when using the recommended columns at a concentration of 10 pg/uL of each of these isomers:

- o unlabeled 2,3,7,8-TCDD
- o $^{13}C_{12}$-2,3,7,8-TCDD
- o 1,2,3,4-TCDD (A)
- o 1,4,7,8-TCDD (A)
- o 1,2,3,7-TCDD (A)
- o 1,2,3,8-TCDD (A)
- o 1,3,6,8-TCDD (F)
- o 1,2,8,9-TCDD (L)

If these solutions are unavailable from EPA, they should be prepared by the analytical laboratory or a chemical supplier and analyzed in a manner traceable to the EPA performance check mixture designed for 2,3,7,8-TCDD monitoring. Similar mixtures of isotopically labeled compounds should be prepared to check performance for monitoring other specific forms of TCDD that are of interest.

8.34 Sample fortification solution - isooctane solution containing the internal standard at a nominal concentration of 10 pg/uL.

8.35 Recovery standard spiking solution - tridecane solution containing the isotopically labeled standard ($^{13}C_{12}$-2,3,7,8-TCDD and other PCDDs of interest) at a concentration of 10.0 pg/uL.

8.36 Field blank fortification solutions - isooctane solutions containing the following:

- Solution A: 10.0 pg/uL of unlabeled 2,3,7,8-TCDD
- Solution B: 10.0 pg/uL of unlabeled 1,2,3,4-TCDD

[NOTE: These reagents and the detailed analytical procedures described herein are designed for monitoring TCDD isomer concentrations of 6.0 pg/m^3 to 37 pg/m^3 each. If ambient concentrations should exceed these levels, concentrations of calibrations and spiking solutions will need to be modified, along with the detailed sample preparation procedures. The reagents and procedures described herein are based on Appendix B of the Protocol for the Analysis of 2,3,7,8-TCDD (Section 2.2.2) combined with the evaluation of the high volume air sampler for PCDD.

9. Preparation of PUF Sampling Cartridge

9.1 The PUF adsorbent is a polyether-type polyurethane foam (density No. 3014 or 0.0225 g/cm^3) used for furniture upholstery.

9.2 The PUF inserts are 6.0-cm diameter cylindrical plugs cut from 3-inch sheet stock and should fit, with slight compression, in the glass cartridge, supported by the wire screen (Figure 1). During cutting, the die is rotated at high speed (e.g., in a drill press) and continuously lubricated with water.

9.3 For initial cleanup, the PUF plug is placed in a Soxhlet apparatus and extracted with acetone for 14-24 hours at approximately 4 cycles per hour. When cartridges are reused, 5% diethyl ether in n-hexane can be used as the cleanup solvent.

9.4 The extracted PUF is placed in a vacuum oven connected to a water aspirator and dried at room temperature for approximately 2-4 hours (until no solvent odor is detected).

9.5 The PUF is placed into the glass sampling cartridge using polyester gloves. The module is wrapped with hexane-rinsed aluminum foil, placed in a labeled container, and tightly sealed.

9.6 At least one assembled cartridge from each batch must be analyzed, as a laboratory blank, using the procedures described in Section 11, before the batch is considered acceptable for field use. A blank level of <10 ng/plug for single compounds is considered to be acceptable.

10. Sample Collection

10.1 Description of Sampling Apparatus

10.1.1 The entire sampling system is diagrammed in Figure 2. A unit specifically designed for this method is commercially available (Model PS-1 - General Metal Works, Inc., Village of Cleves, Ohio).

10.1.2 The sampling module (Figure 1) consists of a glass sampling cartridge and an air-tight metal cartridge holder. The PUF is retained in the glass sampling cartridge.

10.2 Calibration of Sampling System

10.2.1 The airflow through the sampling system is monitored by a Venturi/Magnehelic assembly, as shown in Figure 2. Assembly must be audited every six months using an audit calibration orifice, as described in the U.S. EPA High Volume Sampling Method, 40 CFR 50, Appendix B. A single-point calibration must be performed before and after each sample collection, using the procedure described in Section 10.2.2.

10.2.2 Prior to calibration, a "dummy" PUF cartridge and filter are placed in the sampling head and the sampling motor is activated. The flow control valve is fully opened and the voltage variator is adjusted so that a sample flow rate corresponding to 110% of the desired flow rate is indicated on the Magnehelic (based on the previously obtained multipoint calibration curve). The motor is allowed to warm up for 10 minutes and then the flow control valve is adjusted to achieve the desired flow rate. The ambient temperature and barometric pressure should be recorded on an appropriate data sheet.

10.2.3 The calibration orifice is placed on the sampling head and a manometer is attached to the tap on the calibration orifice. The sampler is momentarily turned off to set the zero level of the manometer. The sampler is then switched on and the manometer reading is recorded after a stable reading is achieved. The sampler is then shut off.

10.2.4 The calibration curve for the orifice is used to calculate sample flow from the data obtained in Section 10.2.3, and the calibration curve for the Venturi/Magnehelic assembly is used to calculate sample flow from the data obtained in Section 10.2.2. The calibration data should be recorded on an appropriate data sheet. If the two values do not agree within 10%, the sampler should be inspected for damage, flow blockage, etc. If no obvious problems are found, the sampler should be recalibrated (multipoint) according to the U.S. EPA High Volume Sampling Method (Section 10.2.1).

10.2.5 A multipoint calibration of the calibration orifice, against a primary standard, should be obtained annually.

10.3 Sample Collection

10.3.1 After the sampling system has been assembled and calibrated as described in Sections 10.1 and 10.2, it can be used to collect air samples, as described in Section 10.3.2.

10.3.2. The samples should be located in an unobstructed area, at least two meters from any obstacle to air flow. The exhaust hose should be stretched out in the downwind direction to prevent recycling of air.

10.3.3 A clean PUF sampling cartridge and quartz filter are removed from sealed transport containers and placed in the sampling head using forceps and gloved hands. The head is tightly sealed into the sampling system. The aluminum foil wrapping is placed back in the sealed container for later use.

10.3.4 The zero reading of the Magnehelic is checked. Ambient temperature, barometric pressure, elapsed time meter setting, sampler serial number, filter number, and PUF cartridge number are recorded on a suitable data sheet, as illustrated in Figure 3.

10.3.5 The voltage variator and flow control valve are placed at the settings used in Section 10.2.3, and the power switch is turned on. The elapsed time meter is activated and the start time is recorded. The flow (Magnehelic setting) is adjusted, if necessary, using the flow control valve.

10.3.6 The Magnehelic reading is recorded every six hours during the sampling period. The calibration curve (Section 10.2.4) is used to calculate the flow rate. Ambient temperature and barometric pressure are recorded at the beginning and end of the sampling period.

10.3.7 At the end of the desired sampling period, the power is turned off and the filter and PUF cartridges are wrapped with the original aluminum foil and placed in sealed, labeled containers for transport back to the laboratory.

10.3.8 The Magnehelic calibration is checked using the calibration orifice, as described in Section 10.2.4. If calibration deviates by more than 10% from the initial reading, the flow data for that sample must be marked as suspect and the sampler should be inspected and/or removed from service.

10.3.9 At least one field filter/PUF blank will be returned to the laboratory with each group of samples. A field blank is treated exactly as a sample except that no air is drawn through the filter/PUF cartridge assembly.

10.3.10 Samples are stored at 20°C in an ice chest until receipt at the analytical laboratory, after which they are refrigerated at 4°C.

11. Sample Extraction

11.1 Immediately before use, charge the Soxhlet apparatus with 200 to 250 mL of benzene and reflux for 2 hours. Let the apparatus cool, disassemble it, transfer the benzene to a clean glass container, and retain it as a blank for later analysis, if required. After sampling, spike the cartridges and filters with an internal standard (Table 1). After spiking, place the PUF cartridge and filter together in the Soxhlet apparatus (the use of an extraction thimble is optional). (The filter and PUF cartridge are analyzed together in order to reach detection limits, avoid questionable interpretation of the data, and minimize cost.) Add 200 to 250 mL of benzene to the apparatus and relux for 18 hours at a rate of at least 3 cycles per hour.

11.2 Transfer the extract to a Kuderna-Danish (K-D) apparatus, concentrate it to 2 to 3 mL, and let it cool. Rinse the column and flask with 5 mL of benzene, collecting the rinsate in the concentrator tube to 2 to 3 mL. Repeat the rinsing and concentration steps twice more. Remove the concentrator tube from the K-D apparatus and carefully reduce the extract volume to approximately 1 mL with a stream of nitrogen using a flow rate and distance above the solution such that a gentle rippling of the solution surface is observed.

11.3 Perform the following column chromatographic procedures for sample extraction cleanup. These procedures have been demonstrated to be effective for a mixture consisting of:

- 1,2,3,4-TCDD
- 1,2,3,4,7,8-H_xCDD
- OCDD
- 2,3,7,8-TCDD

11.3.1 Prepare an acidic silica gel column as follows (Figure 4): Pack a 1 cm x 10 cm chromatographic column with a glass wool plug, a 1-cm layer of Na_2SO_4/K_2CO_3 (1:1), 1.0 g of silica gel (Section 8.6), and 4.0 g of 40-percent (w/w) sulfuric acid-impregnated silica gel (Section 8.7). Pack a second chromatographic column (1 cm x 30 cm) with a glass wool plug and 6.0 g of acidic alumina (Section 8.5), and top it with a 1-cm layer of sodium sulfate (Section 8.30). Add hexane to the columns until they are free of channels and air bubbles.

11.3.2 Quantitatively transfer the benzene extract (1 mL) from the concentrator tub to the top of the silica gel column. Rinse the concentrator tube with 0.5-mL portions of hexane. Transfer the rinses to the top of the silica gel column.

11.3.3 Elute the extract from the silica gel column with 90 of mL hexane directly into a Kudena-Danish concentrator tube. Concentrate the eluate to 0.5 mL, using nitrogen blowdown, as necessary.

11.3.4 Transfer the concentrate (0.5 mL) to the top of the alumina column. Rinse the K-D assembly with two 0.5-mL portions of hexane, and transfer the rinses to the top of the alumina column. Elute the alumina column with 18 mL hexane until the hexane level is just below the top of the sodium sulfate. Discard the eluate. Do not let the columns reach dryness (i.e., maintain a solvent "head").

11.3.5 Place 30 mL of 20% (v/v) methylene chloride in hexane on top of the alumina column and elute the TCDDs from the column. Collect this fraction in a 50-mL Erlenmeyer flask.

11.3.6 Certain extracts, even after cleanup by column chromatography, contain interferences that preclude determination of TCDD at low parts-per-trillion levels. Therefore, a cleanup step is included using activated carbon which selectively retains planar molecules such as TCDDs. The TCDDs are then removed from the carbon by elution with toluene. Proceed as follows: Prepare an 18% Carbopak C/Celite 545® mixture by thoroughly mixing 3.6 grams Carbopak C (80/100 mesh) and 16.4 grams Celite 545® in a 40-mL vial. Activate the mixture at 130°C for 6 hours, and store it in a desiccator. Cut off a clean 5-mL disposable glass pipet at the 4-mL mark. Insert a plug of glass wool (Section 8.1) and push it to the 2-mL mark. Add 340 mg of the activated Carbopak/Celite mixture followed by another glass wool plug. Using two glass rods, push both glass wool plugs simultaneously toward the Carbopak/Celite plug to a length of 2.0 to 2.5 cm. Pre-elute the column with 2 mL of toluene followed by 1 mL of 75:20:5 methylene chloride/methanol/ benzene, 1 mL of 1:1 cyclohexane in methylene choride, and 2 mL of hexane. The flow rate should be less than 0.5 mL per minute. While the column is still wet with hexane, add the entire elute (30 mL) from the alumina column (Section 11.3.5) to the top of the column. Rinse the Erlenmeyer flask that contained the extract twice with 1 mL of hexane and add the rinsates to the top of the column. Elute the column sequentially with two 1-mL aliquots of hexane, 1 mL of 1:1 cyclohexane in methylene chloride, and 1 mL of 75:20:5 methylene chloride/mentanol/benzene. Turn the column upside down and elute the TCDD fraction into a concentrator tube with 6 mL of toluene. Warm the tube to approximately 60°C and reduce the toluene volume to approximately 1 mL using a stream of nitrogen. Carefully transfer the residue into a 1-mL minivial and, again at elevated temperature, reduce the volume to about 100 uL using a stream of nitrogen. Rinse the concentrator tube with 3 washings using 200 uL of 1% toluene in CH_2Cl_2 each time. Add 50 uL of tridecane and store the sample in a refrigerator until GC/MS analysis is performed.

12. HRGC/HRMS System Performance Criteria

The laboratory must document that the system performance criteria specified in Sections 12.1, 12.2, and 12.3 have been met before analysis of samples.

12.1 GC Column Performance

12.1.1 Inject 2 uL of the column performance check solution (Section 8.33) and acquire selected ion monitoring (SIM) data for m/z 258.930, 319.897, 321.894, and 333.933 within a total cycle time of ≤ 1 second.

12.1.2 The chromatographic peak separation between 2,3,7,8-TCDD and the peaks representing any other TCDD isomers must be resolved with a valley of $\leq 25\%$, where

$$\text{Valley Percent} = (x/y)(100)$$

x = measured distance from extroplated baseline to minimum of valley; and

y = the peak height of 2,3,7,8-TCDD.

[Note: It is the responsibility of the laboratory to verify the conditions suitable for the appropriate resolution of 2,3,7,8-TCDD from all other TCDD isomers. The column performance check solution also contains the TCDD isomers eluting first and last under the analytical conditions specified in this protocol, thus defining the retention time window for total TCDD determination. The peaks representing 2,3,7,8-TCDD, and the first and last eluting TCDD isomers must be labeled and identified.]

12.2 Mass Spectometer Performance

12.2.1 The mass spectrometer must be operated in the electron (impact) ionization mode. Static mass resolution of at least 10,000 (10% valley) must be demonstrated before any analysis of a set of samples is performed (Section 12.2.2). Static resolution checks must be performed at the beginning and at the end of each 12-hour period of operation. However, it is recommended that a visual check (e.g., not documented) of the static resolution be made using the peak matching unit before and after each analysis.

12.2.2 Chromatography time for TCDD may exceed the long-term mass stability of the mass spectrometer; therefore, mass drift correction is mandatory. A reference compound (high boiling perfluorokerosene [PFK] is recommended) is introduced into the mass spectrometer. An acceptable lock mass ion at any mass between m/z 250 and m/z 334 (m/z 318.979 from PFK is recommended) must be used to monitor and correct mass drifts.

[NOTE: Excessive PFK may cause background noise problems and contamination of the source, resulting in an increase in "downtime" for source cleaning. Using a PFK molecular leak, tune the instrument to meet the minimum required mass resolution of 10,000 (10% valley) at m/z 254.986 (or any other mass reasonably close to m/z 259). Calibrate the voltage sweep at least across the mass range m/z 259 to m/z 344 and verify that m/z 330.979 from PFK (or any other mass close to m/z 334) is measured within ±5 ppm (i.e., 1.7 mmu). Document the mass resolution by recording the peak profile of the PFK reference peak m/z 318.979 (or any other reference peak at a mass close to m/z 320/322). The format of the peak profile representation must allow manual determination of the resolution;

i.e., the horizontal axis must be a calibrated mass scale (mmu or ppm per division). The result of the peak width measurement (performed at 5 percent of the maximum) must appear on the hard copy and cannot exceed 31.9 mmu or 100 ppm.]

12.3 Initial Calibration

Intitial calibration is required before any samples are analyzed for 2,3,7,8-TCDD. Initial calibration is also required if any routine calibration does not meet the required criteria listed in Section 12.6.

12.3.1 All concentration calibration solutions listed in Table 1 must be utilized for the initial calibration.

12.3.2 Tune the instrument with PFK as described in Section 12.2.2.

12.3.3 Inject 2 uL of the column performance check solution (Section 8.33) and acquire SIM mass spectral data for m/z 258.930, 319.897, 321.894, 331.937, and 333.934 within a total cycle time of ≤ 1 second. The laboratory must not perform any further analysis until it has been demonstrated and documented that the criterion listed in Section 12.1.2 has been met.

12.3.4 Using the same GC (Section 12.1) and MS (Section 12.2) conditions that produced acceptable results with the column performance check solution, analyze a 2-uL aliquot of each of the 5 concentration calibration solutions in triplicate with the gas chromatographic operating parameters shown in Table 2.

12.3.4.1 Total cycle time for data acquisition must be ≤ 1 second. Total cycle time includes the sum of all the dwell times and voltage reset times.

12.3.4.2 Acquire SIM data for the following selected characteristic ions:

m/z	Compound
258.930	TCDD - COCl
319.897	unlabeled TCDD
321.894	unlabeled TCDD
331.937	$^{13}C_{12}$-2,3,7,8-TCDD, $^{13}C_{12}$-1,2,3,4-TCDD
333.934	$^{13}C_{12}$-2,3,7,8-TCDD, $^{13}C_{12}$-1,2,3,4-TCDD

12.3.4.3 The ratio of intergrated ion current for m/z 319.897 to m/z 321.894 for 2,3,7,8-TCDD must be between 0.67 and 0.87 (±13%).

12.3.4.4 The ratio of integrated ion current for m/z 331.937 to m/z 333.934 for $^{13}C_{12}$-2,3,7,8-TCDD and $^{13}C_{12}$-1,2,3,4-TCDD must be between 0.67 and 0.87.

12.3.4.5 Calculate the relative response factor for unlabeled 2,3,7,8-TCDD [RRF(I)] relative to $^{13}C_{12}$-2,3,7,8-TCDD and for labeled $^{13}C_{12}$-2,3,7,8-TCDD [RRF(II)] relative to $^{13}C_{12}$-1,2,3,4-TCDD as follows:

$$RRF(I) = \frac{A_x \cdot Q_{IS}}{Q_x \cdot A_{IS}}$$

$$RRF(II) = \frac{A_{IS} \cdot Q_{RS}}{Q_{IS} \cdot A_{RS}}$$

where:

A_x = sum of the integrated abundances of m/z 319.897 and m/z 321.894 for unlabeled 2,3,7,8,-TCDD.

A_{IS} = sum of the integrated abundances of m/z 331.937 and m/z 333.934 for $^{13}C_{12}$-2,3,7,8-TCDD.

A_{RS} = sum of the integrated abundances for m/z 331.937 and m/z 333.934 for $^{13}C_{12}$-1,2,3,4-TCDD.

Q_{IS} = quantity (pg) of $^{13}C_{12}$-2,3,7,8-TCDD injected.

Q_{RS} = quantity (pg) of $^{13}C_{12}$-1,2,3,4-TCDD injected.

Q_x = quantity (pg) of unlabeled 2,3,7,8-TCDD injected.

12.4 Criteria for Acceptable Calibration

The criteria listed below for acceptable calibration must be met before analysis of any sample is performed.

12.4.1 The percent relative standard deviation (RSD) for the response factors from each of the triplicate analyses for both unlabeled and $^{13}C_{12}$-2,3,7,8-TCDD must be less than $\pm 20\%$.

12.4.2 The variation of the five mean RRFs for unlabeled 2,3,7,8-TCDD obtained from the triplicate analyses must be less than $\pm 20\%$ RSD.

12.4.4 SIM traces for $^{13}C_{12}$-2,3,7,8-TCDD must present a signal-to-noise ratio ≥ 10 for 333.934.

12.4.5 Isotopic ratios (Sections 12.3.4.3 and 12.3.4.4) must be within the allowed range.

[NOTE: If the criteria for acceptable calibration listed in Sections 12.4.1 and 12.4.2 have been met, the RRF can be considered independent of the analyte quantity for the calibration concentration range. The mean RRF from five triplicate determinations for unlabeled 2,3,7,8-TCDD and for $^{13}C_{12}$2,3,7,8-TCDD will be used for all calculations until routine calibration criteria (Section 12.6) are no longer met. At such time, new mean RRFs will be calculated from a new set of five triplicate determinations.]

12.5 Routine Calibration

Routine calibration must be performed at the beginning of each 12-hour period after successful mass resolution and GC column performance check runs.

12.5.1 Inject 2 uL of the concentration calibration solution (Section 8.32) that contains 5.0 pg/uL of unlabeled 2,3,7,8-TCDD, 10.0 pg/uL of $^{13}C_{12}$-2,3,7,8-TCDD, and 5.0 pg/uL $^{13}C_{12}$-1,2,3,4-TCDD. Using the same GC/MS/DS conditions as in Sections 12.1, 12.2, and 12.3, determine and document acceptable calibration as provided in Section 12.6.

12.6 Criteria for Acceptable Routine Calibration

The following criteria must be met before further analysis is performed. If these criteria are not met, corrective action must be taken and the instrument must be recalibrated.

12.6.1 The measured RRF for unlabeled 2,3,7,8-TCDD must be within ±20 percent of the mean values established (Section 12.3.4.5) by triplicate analyses of concentration calibration solutions.

12.6.2 The measured RRF for $^{13}C_{12}$-2,3,7,8-TCDD must be within ±20 percent of the mean value established by triplicate analyses of concentration calibration solutions (Section 12.3.4.5).

12.6.3 Isotopic ratios (Sections 12.3.4.3 and 12.3.4.4) must be within the allowed range.

12.6.4 If one of the above criteria is not satisfied, a second attempt can be made before repeating the entire initialization process (Section 12.3).

[NOTE: An initial calibration must be carried out whenever any HRCC solution is replaced.]

13. Analytical Procedures

13.1 Remove the sample extract or blank from storage, allow it to warm to ambient laboratory temperature, and add 5 uL of recovery standard solution. With a stream of dry, purified nitrogen, reduce the extract/blank volume to 20 uL.

13.2 Inject a 2-uL aliquot of the extract into the GC, which should be operating under the conditions previously used (Section 12.1) to produce acceptable results with the performance check solution.

13.3 Acquire SIM data using the same acquisition time and MS operating conditions previously used (Section 12.3.4) to determine the relative response factors for the following selected characteristic ions:

m/z	Compound
258.930	TCDD - COCl (weak at detection limit level)
319.897	unlabeled TCDD
321.894	unlabeled TCDD
331.937	$^{13}C_{12}$-2,3,7,8-TCDD, $^{13}C_{12}$-1,2,3,4-TCDD,
333.934	$^{13}C_{12}$-2,3,7,8-TCDD, $^{13}C_{12}$-1,2,3,4-TCDD,

13.4 Identification Criteria

13.4.1 The retention time (RT) (at maximum peak height) of the sample component m/z 319.897 must be within -1 to +3 seconds of the retention time of the peak for the isotopically labeled internal standard at m/z 331.937 to attain a positive identification of 2,3,7,8-TCDD. Retention times of other tentatively identified TCDDs must fall within the RT window established by analyzing the column performance check solution (Section 12.1). Retention times are required for all chromatograms.

13.4.2 The ion current responses for m/z 258.930, 319.897 and 321.894 must reach their maxima simultaneously ($\pm$1 scan), and all ion current intensities must be $\geq$2.5 times noise level for positive identification of a TCDD.

13.4.3 The integrated ion current at m/z 319.897 must be between 67 and 87 percent of the ion current response at m/z 321.894.

13.4.4 The integrated ion current at m/z 331.937 must be between 67 and 87 percent of the ion current response at m/z 333.934.

13.4.5 The integrated ion currents for m/z 331.937 and 333.934 must reach their maxima within ±1 scan.

13.4.6 The recovery of the internal standard $^{13}C_{12}$-2,3,7,8-TCDD must be between 40 and 120 percent.

14. Calculations

14.1 Calculate the concentration of 2,3,7,8-TCDD (or any other TCDD isomer) using the formula:

$$C_X = \frac{A_X \cdot Q_{IS}}{A_{IS} \cdot V \cdot \overline{RRF}(I)}$$

where:

C_X = quantity (pg) of unlabeled 2,3,7,8-TCDD (or any other unlabeled TCDD isomer) present.

A_X = sum of the integrated ion abundances determined for m/z 319.897 and 321.894.

A_{IS} = sum of the integrated ion abundances determined for m/z 331.937 and 333.934 of $^{13}C_{12}$-2,3,7,8-TCDD (IS = internal standard).

Q_{IS} = quantity (pg) of $^{13}C_{12}$-2,3,7,8-TCDD added to the sample before extraction (Q_{IS} = 500 pg).

V = volume (m^3) of air sampled.

$\overline{RRF}(I)$ = Calculated mean relative response factor for unlabeled 2,3,7,8-TCDD relative to $^{13}C_{12}$-2,3,7,8-TCDD. This value represents the grand mean of the RRF(I)s obtained in Section 12.3.4.5.

14.2 Calculate the recovery of the internal standard $^{13}C_{12}$-2,3,7,8-TCDD, measured in the sample extract, using the formula:

$$\text{Internal standard, percent recovery} = \frac{A_{IS} \cdot Q_{RS}}{A_{RS} \cdot \overline{RRF}(II) \cdot Q_{IS}} \times 100$$

where:

A_{IS} and Q_{IS} = same definitions as above (Section 14.1)

A_{RS} = sum of the integrated ion abundances determined for m/z 331.937 and 333.934 of $^{13}C_{12}$-1,2,3,4-TCDD (RS = recovery standard).

Q_{RS} = quantity (pg) of $^{13}C_{12}$-1,2,3,4-TCDD added to the sample residue before HRGC-HRMS analysis (Q_{RS} = 500 pg).

RRF(II) = Calculated mean relative response factor for labeled $^{13}C_{12}$-2,3,7,8-TCDD. This value represents the grand mean of the RRF(II)s calculated in Section 12.3.4.5.

14.3 Total TCDD Concentration

14.3.1 All positively identified isomers of TCDD must be within the RT window and meet all identification criteria listed in Sections 13.4.2, 13.4.3, and 13.4.4. Use the expression in Section 14.1 to calculate the concentrations of the other TCDD isomers, with C_X becoming the concentration of any unlabeled TCDD isomer.

14.4 Estimated Detection Limit

14.4.1 For samples in which no unlabeled 2,3,7,8-TCDD was detected, calculate the estimated minimum detectable concentration. The background area is determined by integrating the ion abundances for m/z 319.897 and 321.894 in the appropriate region and relating that height area to an estimated concentration that would produce that product area. Use the formula:

$$CE = \frac{(2.5) \cdot (A_x) \cdot (Q_{IS})}{(A_{IS}) \cdot \overline{RRF}(I) \cdot (W)}$$

where:

C_E = estimated concentration of unlabeled 2,3,7,8-TCDD required to produce A_x.

A_x = sum of integrated ion abundance for m/z 319.897 and 321.894 in the same group of ≥ 25 scans used to measure A_{IS}.

A_{IS} = sum of integrated ion abundance for the appropriate ion characteristic of the internal standard, m/z 331.937 and m/z 333.934.

Q_{IS}, $\overline{RRF}(I)$, and V retain the definitions previously stated in Section 14.1. Alternatively, if peak height measurements are used for quantification, measure the estimated detection limit by the peak height of the noise in the TCDD RT window.

14.5 The relative percent difference (RPD) is calculated as follows:

$$RPD = \frac{|S_1 - S_2|}{(\text{Mean Concentration})} = \frac{|S_1 - S_2|}{(S_1 + S_2)/2} \times 100$$

S_1 and S_2 represent sample and duplicate sample results.

14.6 The total sample volume (V_m) is calculated from the periodic flow readings (Magnehelic) taken in Section 10.3.6 using the following equation:

$$V_m = \frac{Q_1 + Q_2 \cdots Q_N}{N} \times \frac{T}{1000}$$

where:

V_m = total sample volume (m^3).

$Q_1\ Q_2 \cdots Q_N$ = flow rates determined at the beginning, end, and intermediate points during sampling (L/minute).

N = number of data points averaged.

T = elapsed sampling time (minutes).

14.7 The concentration of compound in the sample is calculated using the following equation:

$$V_s = V_m \times \frac{P_A}{760} \times \frac{298}{273 + t_A}$$

where:

V_s = total sample volume (m^3) at 25°C and 760 mm Hg pressure.
V_m = total sample flow (m^3) under ambient conditions.
P_A = ambient pressure (mm Hg).
t_A = ambient temperature (°C).

14.8 The concentration of compound in the sample is calculated using the following equation:

$$C_A = \frac{A \times V_E}{V_i \times V_s}$$

where:

C_A = concentration (ug/m^3) of analyte in the sample.
A = calculated amount of material determined by HRGC/HRMS.
V_i = volume (uL) of extract injected.
V_E = final volume (mL) of extract.
V_s = total volume (m^3) of air samples corrected to standard conditions.

15. Performance Criteria and Quality Assurance

This section summarizes required quality assurance (QA) measures and provides guidance concerning performance criteria that should be achieved within each laboratory.

15.1 Standard Operating Procedures (SOPs)

15.1.1 Users should generate SOPs describing the following activities in their laboratory: 1) assembly, calibration and operation of the sampling system with make and model of equipment used; 2) preparation, purification, storage, and handling of sampling cartridges and filters; 3) assembly, calibration and operation of the HRGC/HRMS system with make and model of equipment used; 4) all aspects of data recording and processing, including lists of computer hardware and software used.

15.1.2 SOPs should provide specific stepwise instructions and should be readily available to and understood by the laboratory personnel conducting the work.

15.2 Process, Field, and Solvent Blanks

15.2.1 One PUF cartridge and filter from each batch of approximately 20 should be analyzed, without shipment to the field, for the compounds of interest to serve as process blank.

15.2.2 During each sampling episode, at least one PUF cartridge and filter should be shipped to the field and returned, without drawing air through the sampler, to serve as a field blank.

15.2.3 During the analysis of each batch of samples, at least one solvent process blank (all steps conducted but no PUF cartridge or filter included) should be carried through the procedure and analyzed.

TABLE 1
COMPOSITION OF CONCENTRATION CALIBRATION SOLUTIONS

	Recovery Standards $^{13}C_{12}$-1,2,3,4-TCDD	Analyte 2,3,7,8-TCDD	Internal Standard $^{13}C_{12}$-2,3,7,8-TCDD
HRCC1	2.5 pg/uL	2.5 pg/uL	10.0 pg/uL
HRCC2	5.0 pg/uL	5.0 pg/uL	10.0 pg/uL
HRCC3	10.0 pg/uL	10.0 pg/uL	10.0 pg/uL
HRCC4	20.0 pg/uL	20.0 pg/uL	10.0 pg/uL
HRCC5	40.0 pg/uL	40.0 pg/uL	10.0 pg/uL

Sample Fortification Solution

5.0 pg/uL of $^{13}C_{12}$-2,3,7,8-TCDD

Recovery Standard Spiking Solution

100 pg/uL $^{13}C_{12}$-1,2,3,4-TCDD

Field Blank Fortification Solutions

A) 4.0 pg/uL of unlabeled 2,3,7,8-TCDD

B) 5.0 pg/uL of unlabeled 1,2,3,4-TCDD

TABLE 2

RECOMMENDED GC OPERATING CONDITIONS

Column coating	SP-2330 (SP 2331)	CP-SIL 88
Film thickness	0.20 um	0.22 um
Column dimensions	60 m x 0.24 mm	50 m x 0.22 mm
Helium linear velocity	28-29 cm/sec at 240°C	28-29 cm/sec at 240°C
Initial temperature	200°C	190°C
Initial time	4 min	3 min
Temperature program	200°C to 250°C at 4°C/min	190°C to 240°C at 5°C/min

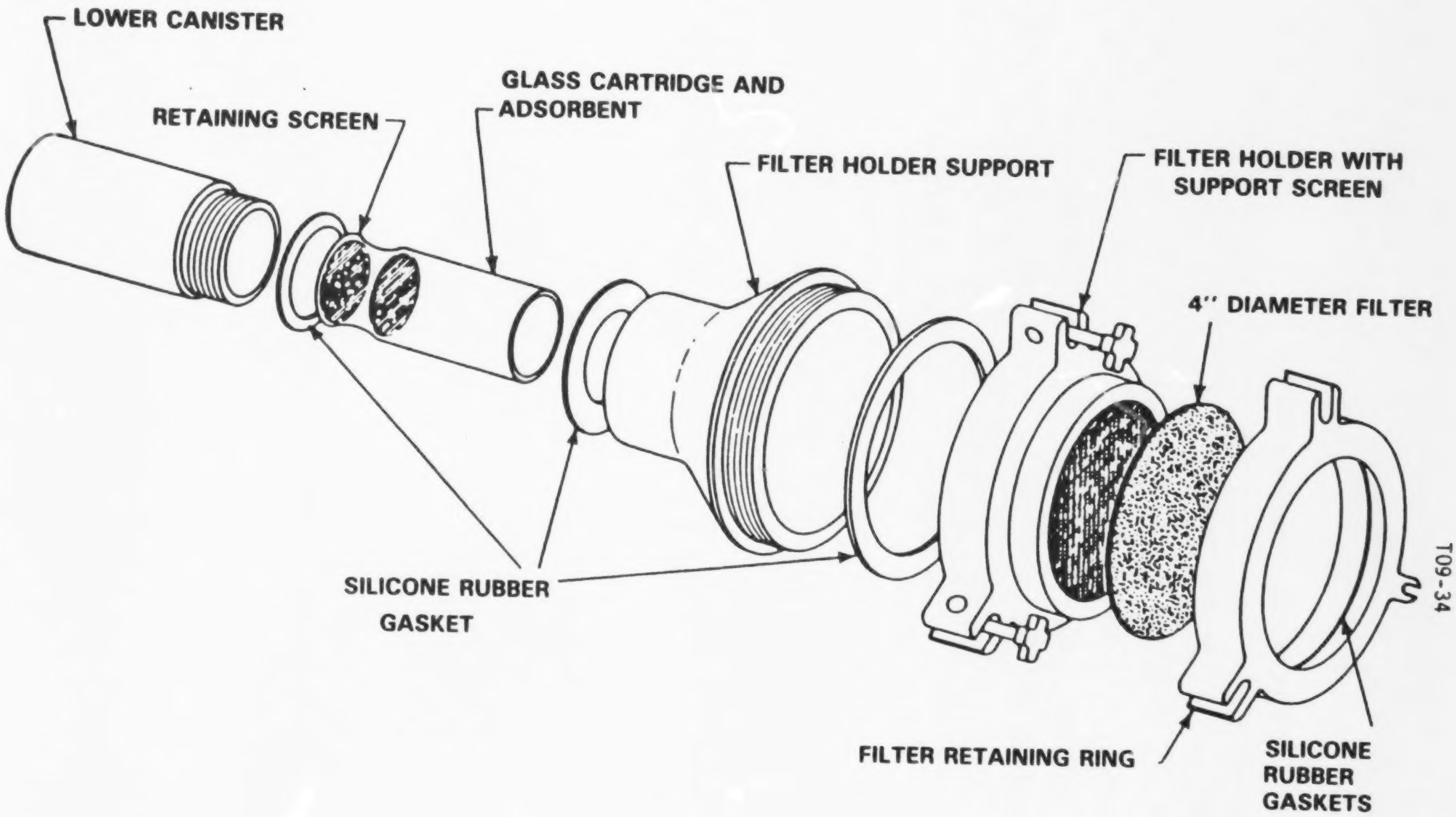

LOWER CANISTER
RETAINING SCREEN
GLASS CARTRIDGE AND ADSORBENT
FILTER HOLDER SUPPORT
FILTER HOLDER WITH SUPPORT SCREEN
4'' DIAMETER FILTER
SILICONE RUBBER GASKET
FILTER RETAINING RING
SILICONE RUBBER GASKETS
T09-34

FIGURE 1. SAMPLING HEAD

T09-35

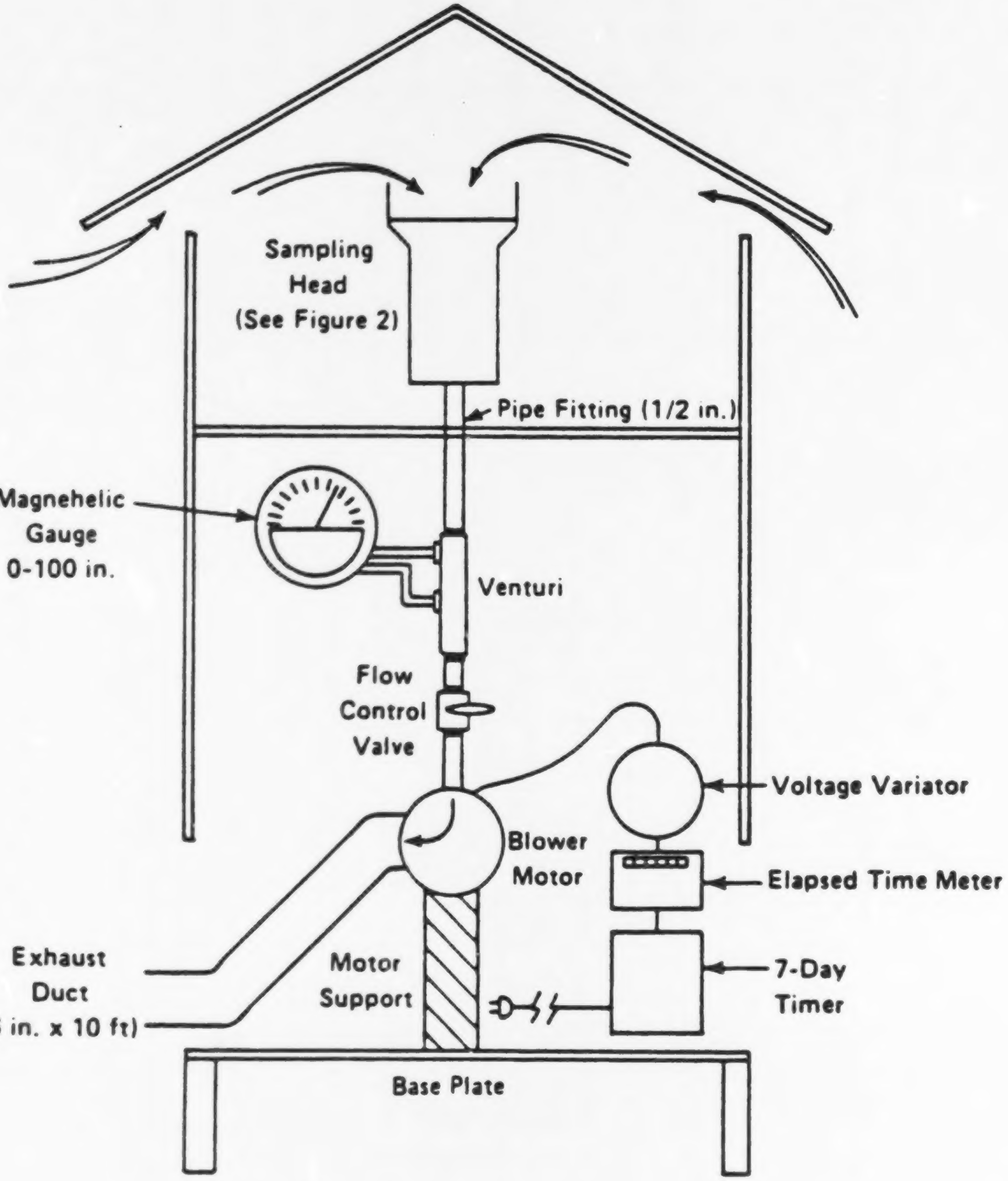

Sampling Head (See Figure 2)
Pipe Fitting (1/2 in.)
Magnehelic Gauge 0-100 in.
Venturi
Flow Control Valve
Voltage Variator
Blower Motor
Elapsed Time Meter
Exhaust Duct (6 in. x 10 ft)
Motor Support
7-Day Timer
Base Plate

FIGURE 2. HIGH VOLUME AIR SAMPLER
GENERAL METAL WORKS (MODEL PS-1)

Performed by_______________ Calibration Orifice S/N____________ Ambient Temperature_________°C

Date/Time_______________ Manometer S/N ________________________ Bar. Press.______________mm Hg

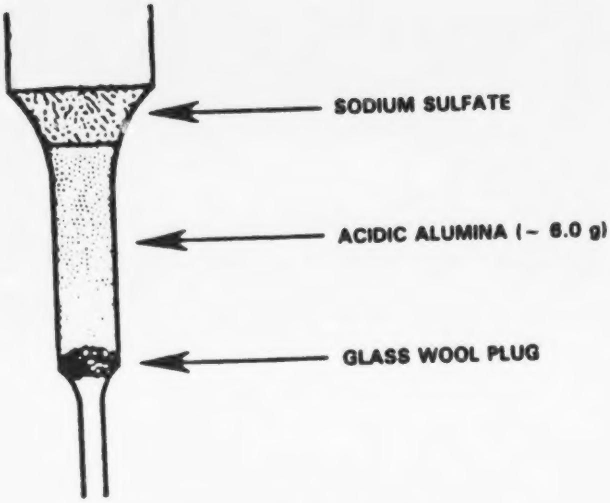
Sampler S/N	Variac Setting V	Timer OK? Yes/No	Calibration Orifice Data		Sampler Venturi Data		% Difference Between Calibration and Sample Venturi Flow Rates	Comments
			Manometer, in. H_2O	Flow Rate scm/min(a)	Magnehelic, in. H_2O	Flow Rate scm/min(b)		

(a) From Calibration Tables for Calibration Orifice or Venturi Tube

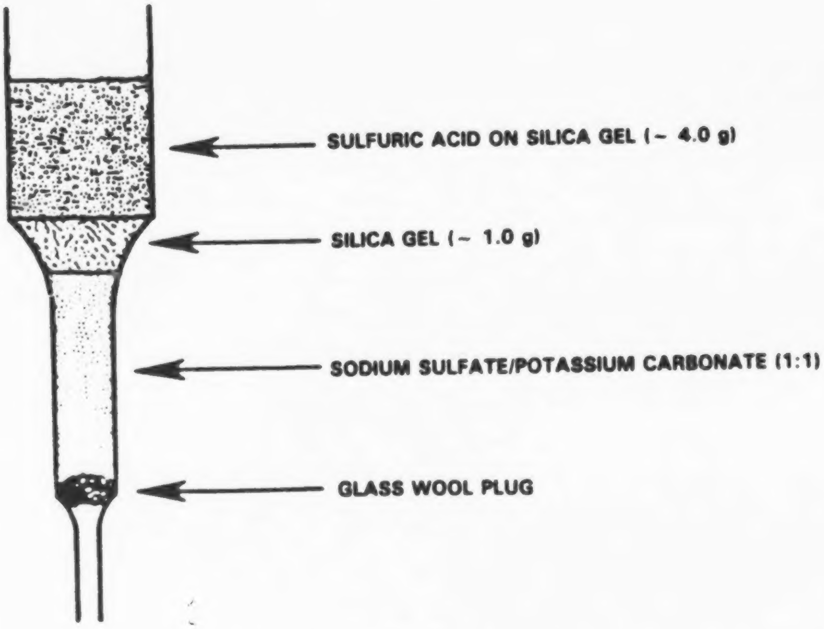
(b) From Calibration Tables for Venturi Tube in each Hi-Vol unit.

Date check by____________ Date ____________

FIGURE 3. EXAMPLE SAMPLING DATA SHEET


SODIUM SULFATE
ACIDIC ALUMINA (~ 6.0 g)
GLASS WOOL PLUG

(a) ALUMINA COLUMN


SULFURIC ACID ON SILICA GEL (~ 4.0 g)
SILICA GEL (~ 1.0 g)
SODIUM SULFATE/POTASSIUM CARBONATE (1:1)
GLASS WOOL PLUG

(b) SILICA GEL COLUMN

FIGURE 4. MULTILAYERED EXTRACT CLEANUP COLUMNS

METHOD TO10 - 1

METHOD FOR THE DETERMINATION OF ORGANOCHLORINE PESTICIDES IN AMBIENT AIR USING LOW VOLUME POLYURETHANE FOAM (PUF) SAMPLING WITH GAS CHROMATOGRAPHY/ELECTRON CAPTURE DETECTOR (GC/ECD)

1. Scope

1.1 This document describes a method for sampling and analysis of a variety of organochlorine pesticides in ambient air. The procedure is based on the adsorption of chemicals from ambient air on polyurethane foam (PUF) using a low volume sampler.

1.2 The low volume PUF sampling procedure is applicable to multicomponent atmospheres containing organochlorine pesticide concentrations from 0.01 to 50 ug/m^3 over 4- to 24-hour sampling periods. The detection limit will depend on the nature of the analyte and the length of the sampling period.

1.3 Specific compounds for which the method has been employed are listed in Table 1. The analysis methodology described in this document is currently employed by laboratories using EPA Method 608. The sampling methodology has been formulated to meet the needs of pesticide sampling in ambient air.

2. Applicable Documents

2.1 ASTM Standards

D1356 - Definitions of Terms Related to Atmospheric Sampling and Analysis.

D1605-60 - Standard Recommended Practices for Sampling Atmospheres for Analysis of Gases and Vapors.

E260 - Recommended Practice for General Gas Chromatography Procedures.

E355 - Practice for Gas Chromatography Terms and Relationships.

2.2 EPA Documents

2.2.1 Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, EPA-600/4-84-041, U.S. Environmental Protection Agency, Research Triangle Park, NC, April 1984.

2.2.2 Manual of Analytical Methods for Determination of Pesticides in Humans and Environmental Standards, EPA-600/8-80-038, U.S. Environmental Protection Agency, Research Triangle Park, NC, July 1982.

2.2.3 "Test Method 608, Organochlorine Pesticides and PCBs," in EPA-600/4-82-057, U. S. Environmental Protection Agency, Cincinnati, Ohio, July 1982.

2.2.4 R. G. Lewis, ASTM draft report on standard practice for sampling and analysis pesticides and polychlorinated biphenyls in indoor atmospheres, U. S. Environmental Protection Agency, Research Triangle Park, NC, June 1987.

3. Summary of Method

3.1 A low volume (1 to 5 L/minute) sampler is used to collect vapors on a sorbent cartridge containing PUF. Airborne particles may also be collected, but the sampling efficiency is not known.

3.2 Pesticides are extracted from the sorbent cartridge with 5% diethyl ether in hexane and determined by gas-liquid chromatography coupled with an electron capture detector (ECD). For some organochlorine pesticides, high performance liquid chromatography (HPLC) coupled with an ultraviolet (UV) detector or electrochemical detector may be preferable. This method describes the use of an electron capture detector.

3.3 Interferences resulting from analytes having similar retention times during gas-liquid chromatography are resolved by improving the resolution or separation, such as by changing the chromatographic column or operating parameters, or by fractionating the sample by column chromatography.

3.4 Sampling procedure is also applicable to other pesticides which may be determined by gas-liquid chromatography coupled with a nitrogen-phosphorus detector (NPD), flame photometric detector (FPD), Hall electrolytic conductivity detector (HECD), or a mass spectrometer (MS).

4. Significance

4.1 Pesticide usage and environmental distribution are common to rural and urban areas of the United States. The application of pesticides can cause adverse health effects to humans by contaminating soil, water, air, plants, and animal life.

4.2 Many pesticides exhibit bioaccumulative, chronic health effects; therefore, monitoring the presence of these compounds in ambient air is of great importance.

4.3 Use of a portable, low volume PUF sampling system allows the user flexibility in locating the apparatus. The user can place the apparatus in a stationary or mobile location. The portable sampling apparatus may be positioned in a vertical or horizontal stationary location (if necessary, accompanied with supporting structure). Mobile positioning of the system can be accomplished by attaching the apparatus to a person to test air in the individual's breathing zone. Moreover, the PUF cartridge used in this method provides for successful collection of most pesticides.

5. Definitions

Definitions used in this document and in any user-prepared Standard Operating Procedures (SOPs) should be consistent with ASTM D1356, D1605-60, E260, and E355. All abbreviations and symbols are defined within this document at point of use.

5.1 Sampling efficiency (SE) - ability of the sampling medium to trap vapors of interest. %SE is the percentage of the analyte of interest collected and retained by the sampling medium when it is introduced as a vapor in air or nitrogen into the air sampler and the sampler is operated under normal conditions for a period of time equal to or greater than that required for the intended use.

5.2 Retention efficiency (RE) - ability of sampling medium to retain a compound added (spiked) to it in liquid solution.

5.2.1 Static retention efficiency - ability of the sampling medium to retain the solution spike when the sampling cartridge is stored under clean, quiescent conditions for the duration of the test period.

5.2.2 Dynamic retention efficiency - ability of the sampling medium to retain the solution spike when air or nitrogen is drawn through the sampling cartridge under normal operating conditions for the duration of the test period. The dynamic RE is normally equal to or less than the SE.

5.3 Retention time (RT) - time to elute a specific chemical from a chromatographic column. For a specific carrier gas flow rate, RT is measured from the time the chemical is injected into the gas stream until it appears at the detector.

5.4 Relative retention time (RRT) - a ratio of RTs for two chemicals for the same chromatographic column and carrier gas flow rate, where the denominator represents a reference chemical.

6. Interferences

6.1 Any gas or liquid chromatographic separation of complex mixtures of organic chemicals is subject to serious interference problems due to coelution of two or more compounds. The use of capillary or narrowbore columns with superior resolution and/or two or more columns of different polarity will frequently eliminate these problems.

6.2 The electron capture detector responds to a wide variety of organic compounds. It is likely that such compounds will be encountered as interferences during GC/ECD analysis. The NPD, FPD, and HECD detectors are element specific, but are still subject to interferences. UV detectors for HPLC are nearly universal, and the electrochemical detector may also respond to a variety of chemicals. Mass spectrometric analyses will generally provide positive identification of specific compounds.

6.3 Certain organochlorine pesticides (e.g., chlordane) are complex mixtures of individual compounds that can make difficult accurate quantification of a particular formulation in a multiple component mixture. Polychlorinated biphenyls (PCBs) may interfere with the determination of pesticides.

6.4 Contamination of glassware and sampling apparatus with traces of pesticides can be a major source of error, particularly at lower analyte concentrations. Careful attention to cleaning and handling procedures is required during all steps of sampling and analysis to minimize this source of error.

6.5 The general approaches listed below should be followed to minimize interferences.

6.5.1 Polar compounds, including certain pesticides (e.g., organophosphorus and carbamate classes), can be removed by column chromatography on alumina. This sample clean-up will permit analysis of most organochlorine pesticides.

6.5.2 PCBs may be separated from other organochlorine pesticides by column chromatography on silicic acid.

6.5.3 Many pesticides can be fractionated into groups by column chromatography on Florisil (Floridin Corp.).

7. Apparatus

7.1 Continuous-flow sampling pump (Figure 1) - (DuPont Alpha-1 Air Sampler, E.I. DuPont de Nemours & Co., Inc., Wilimington, DE, 19898, or equivalent).

7.2 Sampling cartridge (Figure 2) - constructed from a 20 mm (i.d.) x 10 cm borosilicate glass tube drawn down to a 7 mm (o.d.) open connection for attachment to the pump via Tygon tubing (Norton Co., P.O. Box 350, Akron, OH, 44309, or equivalent). The cartridge can be fabricated inexpensively from glass by Kontes (P.O. Box 729, Vineland, NJ, 08360), or equivalent.

7.3 Sorbent, polyurethane foam (PUF) - cut into a cylinder, 22 mm in diameter and 7.6 cm long, fitted under slight compression inside the cartridge. The PUF should be of the polyether type, (density No. 3014 or 0.0225 g/cm^3) used for furniture upholstery, pillows, and mattresses; it may be obtained from Olympic Products Co. (Greensboro, NC), or equivalent source. The PUF cylinders (plugs) should be slightly larger in diameter than the internal diameter of the cartridge. They may be cut by one of the following means:

- With a high-speed cutting tool, such as a motorized cork borer. Distilled water should be used to lubricate the cutting tool.
- With a hot wire cutter. Care should be exercised to prevent thermal degradation of the foam.
- With scissors, while plugs are compressed between the 22 mm circular templates.

Alternatively, pre-extracted PUF plugs and glass cartridges may be obtained commercially (Supelco, Inc., Supelco Park, Bellefonte, PA, 16823, No. 2-0557, or equivalent).

7.4 Gas chromatograph (GC) with an electron capture detector (ECD) and either an isothermally controlled or temperature-programmed heating oven. The analytical system should be complete with all required accessories including syringes, analytical columns, gases, detector, and strip chart recorder. A data system is recommended for measuring peak heights. Consult EPA Method 608 for additional specifications.

7.5 Gas chromatographic column, such as 4- or 2-mm (i.d.) x 183 cm borosilicate glass packed with 1.5% SP-2250 (Supelco, Inc.)/1.95% SP-2401 (Supelco, Inc.) on 100/120 mesh Supelcoport (Supelco, Inc.), 4% SE-30 (General Electric, 50 Fordham Rd., Wilmington, MA, 01887, or equivalent)/6% OV-210 (Ohio Valley Specialty Chemical, 115 Industry Rd., Marietta, OH, 45750, or equivalent) on 100/200 mesh Gas Chrom Q (Alltec Assoc., Applied Science Labs, 2051 Waukegan Rd, Deerfield, IL, 60015, or equivalent), 3% OV-101 (Ohio Valley Specialty Chemical) on UltraBond (Ultra Scientific, 1 Main St., Hope, RI, 02831, or equivalent) and 3% OV-1 (Ohio Valley Specialty Chemical) on 80/100 mesh Chromosorb WHP (Manville, Filtration, and Materials, P.O. Box 5108, Denver CO, 80271, or equivalent). Capillary GC column, such as 0.32 mm (i.d.) x 30 m DB-5 (J&W Scientific, 3871 Security Park Dr., Rancho Cordova, CA, 95670, or equivalent) with 0.25 um film thickness. HPLC column, such as 4.6 mm x 25 cm Zorbax SIL (DuPont Co., Concord Plaza, Wilmington, DE, 19898, or equivalent) or u-Bondapak C-18 (Millipore Corp., 80 Ashby Rd., Bedfore, MA, 01730, or equivalent).

7.6 Microsyringes - 5 uL volume or other appropriate sizes.

8. Reagents and Materials

[Note: For a detailed listing of various other items required for extract preparation, cleanup, and analysis, consult U.S. Method 608 which is provided in Appendix A of Method TO-4 in the Compendium.]

8.1 Round bottom flasks, 500 mL, Ŧ 24/40 joints.

8.2 Soxhlet extractors, 300 mL, with reflux condensers.

8.3 Kuderna-Danish concentrator apparatus, 500 mL, with Snyder columns.

8.4 Graduated concentrator tubes, 10 mL, with Ŧ 19/22 stoppers (Kontes, P.O. Box 729, Vineland, NJ, 08360, Cat. No. K-570050, size 1025, or equivalent).

8.5 Graduated concentrator tubes, 1 mL, with Ŧ 14/20 stoppers (Kontes, Vineland, NJ, Cat. No. K-570050, size 0124, or equivalent).

8.6 TFE fluorocarbon tape, 1/2 in.

8.7 Filter tubes, size 40 mm (i.d.) x 80 mm, (Corning Glass Works, Science Products, Houghton Park, AB-1, Corning, NY, 14831, Cat. No. 9480, or equivalent).

8.8 Serum vials, 1 mL and 5 mL, fitted with caps lined with TFE fluorocarbon.

8.9 Pasteur pipettes, 9 in.

8.10 Glass wool fired at 500°C.

8.11 Boiling chips fired at 500°C.

8.12 Forceps, stainless steel, 12 in.

8.13 Gloves, latex or precleaned (5% ether/hexane Soxhlet extracted) cotton.

8.14 Steam bath.

8.15 Heating mantles, 500 mL.

8.16 Analytical evaporator, nitrogen blow-down (N-Evap®, Organomation Assoc., P.O. Box 159, South Berlin, MA, 01549, or equivalent).

8.17 Acetone, pesticide quality.

8.18 n-Hexane, pesticide quality.

8.19 Diethyl ether preserved with 2% ethanol (Mallinckrodt, Inc., Science Products Division, P.O. Box 5840, St. Louis, MO, 63134, Cat. No. 0850, or equivalent).

8.20 Sodium sulfate, anhydrous analytical grade.

8.21 Alumina, activity grade IV, 100/200 mesh.

8.22 Glass chromatographic column (2 mm i.d. x 15 cm long).

8.23 Soxhlet extraction system, including Soxhlet extractors (500 and 300 mL), variable voltage transformers, and cooling water source.

8.24 Vacuum oven connected to water aspirator.

8.25 Die.

8.26 Ice chest.

8.27 Silicic acid, pesticide quality.

8.28 Octachloronaphthalene (OCN), research grade, (Ultra Scientific, Inc., 1 Main St., Hope, RI, 02831, or equivalent).

8.29 Florisil (Floridin Corp.).

9. Assembly and Calibration of Sampling System

9.1 Description of Sampling Apparatus

9.1.1 The entire sampling system is diagrammed in Figure 1. This apparatus was developed to operate at a rate of 1-5 L/minute and is used by U.S. EPA for low volume sampling of ambient air. The method writeup presents the use of this device.

9.1.2 The sampling module (Figure 2) consists of a glass sampling cartridge in which the PUF plug is retained.

9.2 Calibration of Sampling System

9.2.1 Air flow through the sampling system is calibrated by the assembly shown in Figure 3. The air sampler must be calibrated in the laboratory before and after each sample collection period, using the procedure described below.

9.2.2 For accurate calibration, attach the sampling cartridge in-line during calibration. Vinyl bubble tubing (Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA, 15219, Cat. No. 14-170-132, or equivalent) or other means (*e.g.*, rubber stopper or glass joint) may be used to connect the large end of the cartridge to the calibration system. Refer to ASTM Standard Practice D3686, Annex A2 or Standard Practice D4185, Annex A1 for procedures to calibrate small volume air pumps.

10. Preparation of Sampling (PUF) Cartridges

10.1 The PUF adsorbent is white and yellows upon exposure to light.

10.2 For initial cleanup and quality assurance purposes, the PUF plug is placed in a Soxhlet extractor and extracted with acetone for 14 to 24 hours at 4 to 6 cycles per hour (If commercially pre-extracted PUF plugs are used, extraction with acetone is not required.). This procedure is followed by a 16-hour Soxhlet extraction with 5% diethyl ether in n-hexane. When cartridges are reused, 5% ether in n-hexane can be used as the cleanup solvent.

10.3 The extracted PUF is placed in a vacuum oven connected to a water aspirator and dried at room temperature for 2 to 4 hours (until no solvent odor is detected). The clean PUF is placed in labeled glass sampling cartridges using gloves and forceps. The cartridges are wrapped with hexane-rinsed aluminum foil and placed in glass jars fitted with TFE fluorocarbon-lined caps. The foil wrapping may also be marked for identification using a blunt probe.

10.4 At least one assembled cartridge from each batch should be analyzed as a laboratory blank before any samples are analyzed. A blank level of <10 ng/plug for single component compounds is considered to be acceptable. For multiple component mixtures, the blank level should be <100 ng/plug.

11. Sampling

11.1 After the sampling system has been assembled and calibrated as per Section 9, it can be used to collect air samples as described below.

11.2 The prepared sample cartridges should be used within 30 days of loading and should be handled only with latex or precleaned cotton gloves.

11.3 The clean sample cartridge is carefully removed from the aluminum foil wrapping (the foil is returned to jars for later use) and attached to the pump with flexible tubing. The sampling assembly is positioned with the intake downward or horizontally. The sampler is located in an unobstructed area at least 30 cm from any obstacle to air flow. The PUF cartridge intake is positioned 1 to 2 m above ground level. Cartridge height above ground is recorded on the Sampling Data Form shown in Figure 4.

11.4 After the PUF cartridge is correctly inserted and positioned, the power switch is turned on and the sampling begins. The elapsed time meter is activated and the start time is recorded. The pumps are checked during the sampling process and any abnormal conditions discovered are recorded on the data sheet. Ambient temperatures and barometric pressures are measured and recorded periodically during the sampling procedure.

11.5 At the end of the desired sampling period, the power is turned off and the PUF cartridges are wrapped with the original aluminum foil and placed in sealed, labeled containers for transport back to the laboratory. At least one field blank is returned to the laboratory with each group of samples. A field blank is treated exactly like a sample except that no air is drawn through the cartridge. Samples are stored at -10°C or below until analyzed.

12. Sample Preparation, Cleanup, and Analysis

[Note: Sample preparation should be preformed under a properly ventilated hood.]

12.1 Sample Preparation

12.1.1 All samples should be extracted within 1 week after collection.

12.1.2 All glassware is washed with a suitable detergent; rinsed with deionized water, acetone, and hexane; rinsed again with deionized water; and fired in an oven (450°C).

12.1.3 Sample extraction efficiency is determined by spiking the samples with a known solution. Octachloronaphthalene (OCN) is an appropriate standard to use for pesticide analysis using GC/ECD techniques. The spiking solution is prepared by dissolving 10 mg of OCN in 10 mL of 10% acetone in n-hexane, followed by serial dilution with n-hexane to achieve a final concentration of 1 ug/mL.

12.1.4 The extracting solution (5% ether/hexane) is prepared by mixing 1900 mL of freshly opened hexane and 100 mL of freshly opened ethyl ether (preserved with ethanol) to a flask.

12.1.5 All clean glassware, forceps, and other equipment to be used are placed on rinsed (5% ether/hexane) aluminum foil until use. The forceps are also rinsed with 5% ether/hexane. The condensing towers are rinsed with 5% ether/hexane and 300 mL are added to a 500 mL round bottom boiling flask.

12.1.6 Using precleaned (e.g., 5% ether/hexane Soxhlet extracted) cotton gloves, the PUF cartridges are removed from the sealed container and the PUF is placed into a 300 mL Soxhlet extractor using prerinsed forceps.

12.1.7 Before extraction begins, 100 uL of the OCN solution are added directly to the top of the PUF plug. Addition of the standard demonstrates extraction efficiency of the Soxhlet procedure. [Note: Incorporating a known concentration of the solution onto the sample provides a quality assurance check to determine recovery efficiency of the extraction and analytical processes.]

12.1.8 The Soxhlet extractor is then connected to the 500 mL boiling flask and condenser. The glass joints of the assembly are wet with 5% ether/hexane to ensure a tight seal between the fittings. If necessary, the PUF plug can be adjusted using forceps to wedge it midway along the length of the siphon. The above procedure should be followed for all samples, with the inclusion of a blank control sample.

12.1.9 The water flow to the condenser towers of the Soxhlet extraction assembly is checked and the heating unit is turned on. As the samples boil, the Soxhlet extractors are inspected to ensure that they are filling and siphoning properly (4 to 6 cycles/hour). Samples should cycle for a minimum of 16 hours.

12.1.10 At the end of the extracting process, the heating units are turned off and the samples are cooled to room temperature.

12.1.11 The extracts are concentrated to a 5 mL solution using a Kuderna-Danish (K-D) apparatus. The K-D is set up and assembled with concentrator tubes. This assembly is rinsed. The lower end of the filter tube is packed with glass wool and filled with sodium sulfate to a depth of 40 mm. The filter tube is placed in the neck of the K-D. The Soxhlet extractors and boiling flasks are carefully removed from the condenser towers and the remaining solvent is drained into each boiling flask. Sample extract is carefully poured through the filter tube into the K-D. Each boiling flask is rinsed three times by swirling hexane along the sides. Once the sample has drained, the filter tube is rinsed down with hexane. Each Synder column is attached to the K-D and rinsed to wet the joint for a tight seal. The complete K-D apparatus is placed on a steam bath and the sample is evaporated to approximately 5 mL. The sample is removed from the steam bath and allowed to cool. Each Synder column is rinsed with a minimum of hexane. Sample volume is adjusted to 10 mL in a concentrator tube, which is then closed with a glass stopper and sealed with TFE fluorocarbon tape. Alternatively, the sample may be quantitatively transferred (with concentrator tube rinsing) to prescored vials and brought up to final volume. Concentrated extracts are stored at -10°C until analyzed. Analysis should occur no later than two weeks after sample extraction.

12.2 Sample Cleanup

12.2.1 If only organochlorine pesticides are sought, an alumina cleanup procedure is appropriate. Before cleanup, the sample extract is carefully reduced to 1 mL using a gentle stream of clean nitrogen.

12.2.2 A glass chromatographic column (2 mm i.d. x 15 cm long) is packed with alumina, activity grade IV, and rinsed with approximately 20 mL of n-hexane. The concentrated sample extract is placed on the column and eluted with 10 mL of n-hexane at a rate of 0.5 mL/minute. The eluate volume is adjusted to exactly 10 mL and analyzed as per 12.3.

12.2.3 If other pesticides are sought, alternate cleanup procedures may be required (e.g., Florisil). EPA Method 608 identifies appropriate cleanup procedures.

12.3 Sample Analysis

12.3.1 Organochlorine pesticides and many nonchlorinated pesticides are responsive to electron capture detection (Table 1). Most of these compounds can be determined at concentrations of 1 to 50 ng/mL by GC/ECD.

12.3.2 An appropriate GC column is selected for analysis of the extract. (For example, 4 mm i.d. x 183 cm glass, packed with 1.5% SP-2250/1.95% SP-2401 on 100/120 mesh Supelo-port, 200°C isothermal, with 5% methane/95% argon carrier gas at 65 to 85 mL/min). A chromatogram showing a mixture containing single component pesticides determined by GC/ECD using a packed column is shown in Figure 5. A table of corresponding chromatographic characteristics follows in Figure 6.

12.3.3 A standard solution is prepared from reference materials of known purity. Standards of organochlorine pesticides may be obtained from the National Bureau of Standards and from the U.S. EPA.

12.3.4 Stock standard solutions (1.00 ug/uL) are prepared by dissolving approximately 10 milligrams of pure material in isooctane and diluting to volume in a 10 mL volumetric flask. Larger volumes can be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commerically prepared stock standards may be used at any concentration if they are certified by the manufacturer or an independent source.

12.3.5 The prepared stock standard solutions are transferred to Teflon-sealed screw-capped bottles and stored at -10°C for no longer than six months. The standard solutions should be inspected frequently for signs of degradation or evaporation (especially before preparing calibration standards from them). [Note: Quality control check standards used to determine accuracy of the calibration standards are available from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.]

12.3.6 The standard solutions of the various compounds of interest are used to determine relative retention times (RRTs) to an internal standard such as p,p'-DDE, aldrin, or OCN.

12.3.7 Before analysis, the GC column is made sensitive to the pesticide samples by injecting a standard pesticide solution ten (10) times more concentrated than the stock standard solution. Detector linearity is then determined by injecting standard solutions of three different concentrations that bracket the required range of analyses.

12.3.8 The GC system is calibrated daily with a minimum of three injections of calibrated standards. Consult EPA Method 608, Section 7 for a detailed procedure to calibrate the gas chromatograph.

12.3.9 If refrigerated, the sample extract is removed from the cooling unit and allowed to warm to room temperature. The sample extract is injected into the GC for analysis in an aliquot of approximately 2-6 uL using the solvent-flush technique (Ref. D3687, 8.1.4.3-8.1.4.5). The actual volume injected is recorded to the nearest 0.05 uL. After GC injection, the sample's response from the strip chart is analyzed by measuring peak heights or determining peak areas. Ideally, the peak heights should be 20 to 80% of full scale deflection. Using injections of 2 to 6 uL of each calibration standard, the peak height or area responses are tabulated against the mass injected (injections of 2, 4, and 6 uL are recommended). If the response (peak height or area) exceeds the linear range of detection, the extract is diluted and reanalyzed.

12.3.10 Pesticide mixtures are quantified by comparison of the total heights or areas of GC peaks with the corresponding peaks in the best-matching standard. If both PCBs and organochlorine pesticides are present in the same sample, column chromatographic separation on silicic acid is used before GC analysis, according to ASTM Standards, Vol. 14.01. If polar compounds that interfere with GC/ECD analysis are present, column chromatographic cleanup on alumina (activity grade IV) is used as per Section 12.2.2.

12.3.11 For confirmation, a second GC column is used such as 4% SE-30/6% OV-210 on 100/200 mesh Gas Chrom Q or 3% OV-1 on 80/100 mesh Chromosorb WHP. For improved resolution, a capillary column is used such as 0.32 mm (i.d.) x 30 m DB-5 with 0.25 um film thickness.

12.3.12 A chromatogram of a mixture containing single component pesticides determined by GC/ECD using a capillary column is shown in Figure 7. A table of the corresponding chromatographic characteristics follows in Figure 8.

12.3.13 Class separation and improved specificity can be achieved by column chromatographic separation on Florisil as per EPA Method 608. For improved specificity, a Hall electrolytic conductivity detector operated in the reductive mode may be substituted for the electron capture detector. Limits of detection will be reduced by at least an order of magnitude, however.

13. GC Calibration

Appropriate calibration procedures are identified in EPA Method 608, Section 7.

14. Calculations

14.1 The concentration of the analyte in the extract solution is taken from a standard curve where peak height or area is plotted linearly against concentration in nanograms per milliliter (ng/mL). If the detector response is known to be linear, a single point is used as a calculation constant.

14.2 From the standard curve, determine the ng of analyte standard equivalent to the peak height or area for a particular compound.

14.3 Determine if the field blank is contaminated. Blank levels should not exceed 10 ng/sample for organochlorine pesticides or 100 ng/sample for other pesticides. If the blank has been contaminated, the sampling series must be held suspect.

14.4 Quantity of the compound in the sample (A) is calculated using the following equation:

$$A = 1000 \left(\frac{A_s \times V_e}{V_i} \right)$$

where:

A = total amount of analyte in the sample (ng).

A_s = calculated amount of material (ng) injected onto the chromatograph based on calibration curve for injected standards

V_e = final volume of extract (mL).

V_i = volume of extract injected (uL).

1000 = factor for converting microliters to milliliters.

14.5 The extraction efficiency (EE) is determined from the recovery of octachloronaphthalene (OCN) spike as follows:

$$EE(\%) = \frac{S}{S_a} \times 100$$

where:

S = amount of spike (ng) recovered.

S_a = amount of spike (ng) added to plug.

14.6 The total amount of nanograms found in the sample is corrected for extraction efficiency and laboratory blank as follows:

$$A_c = \frac{A - A_o}{EE\ (\%)}$$

where:

A_c = corrected amount of analyte in sample (ng).

A_o = amount of analyte in blank (ng).

14.7 The total volume of air sampled under ambient conditions is determined using the following equation:

$$V_a = \frac{\sum_{i=1}^{n} (T_i \times F_i)}{1000\ L/m^3}$$

where:

V_a = total volume of air sampled (m^3).
T_i = length of sampling segment (min) between flow checks.
F_i = average flow (L/min) during sampling segment.

14.8 The air volume is corrected to 25° and 760 mm Hg (STP) as follows:

$$V_s = V_a \left(\frac{P_b - P_w}{760\ \text{mm Hg}} \right) \cdot \left(\frac{298\ K}{t_A} \right)$$

where:

V_s = volume of air (m^3) at standard conditions.
V_a = total volume of air sampled (m^3).
P_b = average ambient barometric pressure (mm Hg).
P_w = vapor pressure of water (mm Hg) at calibration temperature.
t_A = average ambient temperature (K).

14.9 If the proper criteria for a sample have been met, concentration of the compound in a cubic meter of air is calculated as follows:

$$ng/m^3 = \frac{A_c}{V_s} \times \frac{100}{SE(\%)}$$

where:

SE = sampling efficiency as determined by the procedure outlined in Section 15.

If it is desired to convert the air concentration value to parts per trillion (wt/wt) in dry air at STP, the following conversion is used:

$$ppt = 1.205\ ng/m^3$$

The air concentration is converted to parts per trillion (v/v) in air at STP as follows:

$$\text{pptv} = 24.45 \left(\frac{\text{ng/m}^3}{\text{MW}}\right)$$

where:

MW = molecular weight of the compound of interest.

15. Sampling and Retention Efficiencies

15.1 Before using this procedure, the user should determine the sampling efficiency for the compound of interest. The sampling efficiencies shown in Tables 2 and 3 were determined for approximately 1 m^3 of air at about 25°C, sampled at 3.8 L/min. Sampling efficiencies for the pesticides shown in Table 4 are for 24 hours at 3.8 L/min and 25°C. For compounds not listed, longer sampling times, different flow rates, or other air temperatures, the following procedure may be used to determine sampling efficiencies.

15.2 SE is determined by a modified impinger assembly attached to the sampler pump (Figure 9). Clean PUF is placed in the pre-filter location and the inlet is attached to a nitrogen line. [Note: Nitrogen should be used instead of air to prevent oxidation of the compounds under test. The oxidation would not necessarily reflect what may be encountered during actual sampling and may give misleading sampling efficiencies.] PUF plugs (22 mm x 7.6 cm) are placed in the primary and secondary traps and are attached to the pump.

15.3 A standard solution of the compound of interest is prepared in a volatile solvent (e.g., hexane, pentane, or benzene). A small, accurately measured volume (e.g., 1 mL) of the standard solution is placed into the modified midget impinger. The sampler pump is set at the rate to be used in field application and then activated. Nitrogen is drawn through the assembly for a period of time equal to or exceeding that intended for field application. After the desired sampling test period, the PUF plugs are removed and analyzed separately as per Section 12.3.

15.4 The impinger is rinsed with hexane or another suitable solvent and quantitatively transferred to a volumetric flask or concentrator tube for analysis.

15.5 The sampling efficiency (SE) is determined using the following equation:

$$\% \text{ SE} = \frac{W_1}{W_0 - W_r} \times 100$$

where:

W_1 = amount of compound extracted from the primary trap (ng).
W_0 = original amount of compound added to the impinger (ng).
W_r = residue left in the impinger at the end of the test (ng)

15.6 If material is found in the secondary trap, it is an indication that breakthrough has occurred. The addition of the amount found in the secondary trap, W_2, to W_1, will provide an indication of the overall sampling efficiency of a tandem-trap sampling system. The sum of W_1, W_2 (if any), and W_r must equal (approximately ± 10%) W_0 or the test is invalid.

15.7 If the compound of interest is not sufficiently volatile to vaporize at room temperature, the impinger may be heated in a water bath or other suitable heater to a maximum of 50°C to aid volatilization. If the compound of interest cannot be vaporized at 50°C or without thermal degradation, dynamic retention efficiency (RE_d) may be used to estimate sampling efficiency. Dynamic retention efficiency is determined in the manner described in 15.8. Table 5 lists those organochlorine pesticides which dynamic retention efficiencies have been determined.

15.8 A pair of PUF plugs is spiked by slow, dropwise addition of the standard solution to one end of each plug. No more than 0.5 to 1 mL of solution should be used. Amounts added to each plug should be as nearly the same as possible. The plugs are allowed to dry for 2 hours in a clean, protected place (e.g., dessicator). One spiked plug is placed in the primary trap so that the spiked end is at the intake and one clean unspiked plug is placed in the secondary trap. The other spiked plug is wrapped in hexane-rinsed aluminum foil and stored in a clean place for the duration of the test (this is the static control plug, Section 15.9). Prefiltered nitrogen or ambient air is drawn through the assembly as per Section 15.3. [Note: Impinger may be discarded.] Each PUF plug (spiked and static control) is analyzed separately as per Section 12.3.

15.9 % RE_d is calculated as follows:

$$\% \; RE_d = \frac{W_1}{W_o} \times 100$$

where:

W_1 = amount of compound (ng) recovered from primary plug.

W_o = amount of compound (ng) added to primary plug.

If a residue, W_2, is found on the secondary plug, breakthrough has occurred. The sum of $W_1 + W_2$ must equal W_o, within 25% or the test is invalid. For most compounds tested by this procedure, % RE_d values are generally less than % SE values determined per Section 15.1. The purpose of the static RE_d determination is to establish any loss or gain of analyte unrelated to the flow of nitrogen or air through the PUF plug.

16. Performance Criteria and Quality Assurance

This section summarizes required quality assurance (QA) measures and provides guidance concerning performance criteria that should be achieved within each laboratory.

16.1 Standard Operating Procedures (SOPs)

16.1.1 Users should generate SOPs describing the following activities accomplished in their laboratory: (1) assembly, calibration, and operation of the sampling system, with make and model of equipment used; (2) preparation, purification, storage, and handling of sampling cartridges, (3) assembly, calibration, and operation of the GC/ECD system, with make and model of equipment used; and (4) all aspects of data recording and processing, including lists of computer hardware and software used.

16.1.2 SOPs should provide specific stepwise instructions and should be readily available to, and understood by, the laboratory personnel conducting the work.

16.2 Process, Field, and Solvent Blanks

16.2.1 One PUF cartridge from each batch of approximately twenty should be analyzed, without shipment to the field, for the compounds of interest to serve as a process blank.

16.2.2 During each sampling episode, at least one PUF cartridge should be shipped to the field and returned, without drawing air through the sampler, to serve as a field blank.

16.2.3 Before each sampling episode, one PUF plug from each batch of approximately twenty should be spiked with a known amount of the standard solution. The spiked plug will remain in a sealed container and will not be used during the sampling peroid. The spiked plug is extracted and analyzed with the other samples. This field spike acts as a quality assurance check to determine matrix spike recoveries and to indicate sample degradation.

16.2.4 During the analysis of each batch of samples, at least one solvent process blank (all steps conducted but no PUF cartridge included) should be carried through the procedure and analyzed.

16.2.5 Blank levels should not exceed 10 ng/sample for single components or 100 ng/sample for multiple component mixtures (e.g., for organochlorine pesticides).

16.3 Sampling Efficiency and Spike Recovery

16.3.1 Before using the method for sample analysis, each laboratory must determine its sampling efficiency for the component of interest as per Section 15.

16.3.2 The PUF in the sampler is replaced with a hexane-extracted PUF. The PUF is spiked with a microgram level of compounds of interest by dropwise addition of hexane solutions of the compounds. The solvent is allowed to evaporate.

16.3.3 The sampling system is activated and set at the desired sampling flow rate. The sample flow is monitored for 24 hours.

16.3.4 The PUF cartridge is then removed and analyzed as per Section 12.3.

16.3.5 A second sample, unspiked, is collected over the same time period to account for any background levels of components in the ambient air matrix.

16.3.6 In general, analytical recoveries and collection efficiencies of 75% are considered to be acceptable method performance.

16.3.7 Replicate (at least triplicate) determinations of collection efficiency should be made. Relative standard deviations for these replicate determinations of ±15% or less are considered acceptable performance.

16.3.8 Blind spiked samples should be included with sample sets periodically as a check on analytical performance.

16.4 Method Precision and Accuracy

16.4.1 Several different parameters involved in both the sampling and analysis steps of this method collectively determine the accuracy with which each compound is detected. As the volume of air sampled is increased, the sensitivity of detection increases proportionately within limits set by (a) the retention efficiency for each specific component trapped on the polyurethane foam plug, and (b) the background interference associated with the analysis of each specific component at a given site sampled. The accuracy of detection of samples recovered by extraction depends on (a) the inherent response of the particular GC detector used in the determinative step, and (b) the extent to which the sample is concentrated for analysis. It is the responsibility of the analyst(s) performing the sampling and analysis steps to adjust parameters so that the required detection limits can be obtained.

16.4.2 The reproducibility of this method has been determined to range from ±5 to ±30% (measured as the relative standard deviation) when replicate sampling cartridges are used (N>5). Sample recoveries for individual compounds generally fall within the range of 90 to 110%, but recoveries ranging from 75 to 115% are considered acceptable. PUF alone may give lower recoveries for more volatile compounds (e.g., those with saturation vapor pressures $>10^{-3}$ mm Hg). In those cases, another sorbent or a combination of PUF and Tenax GC should be employed.

16.5 Method Safety

This procedure may involve hazardous materials, operations, and equipment. This method does not purport to address all of the safety problems associated with its use. It is the users responsibility to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to the implementation of this procedure. This should be part of the users SOP manual.

TABLE 1. PESTICIDES DETERMINED BY GAS CHROMATOGRAPHY/ELECTRON CAPTURE DETECTOR (GC/ECD)

Aldrin
BHC (α- and β-Hexachlorocyclohexanes)
Captan
Chlordane, technical
Chlorothalonil
Chlorpyrifos
2,4,-D esters
p,*p*,-DDT
p,*p*,-DDE
Dieldrin
Dichlorvos (DDVP)
Dicofol
Endrin
Endrin aldehyde
Folpet
Heptachlor
Heptachlor epoxide
Hexachlorobenzene
Lindane (γ-BHC)
Methoxychlor
Mexacarbate
Mirex
trans-Nonachlor
Oxychlordane
Pentachlorobenzene
Pentachlorophenol
Ronnel
2,4,5-Trichlorophenol

TABLE 2. SAMPLING EFFICIENCIES FOR SOME ORGANOCHLORINE PESTICIDES

Compound	Quantity Introduced, ug	Air Volume, m^3	Sampling Efficiency, %		
			mean	RSD	n
α-Hexachlorocyclohexane (α-BHC)	0.005	0.9	115	8	6
γ-Hexachlorocyclohexane (Lindane)	0.05-1.0	0.9	91.5	8	5
Hexachlorobenzene †	0.5, 1.0	0.9	94.5	8	5
Chlordane, technical	0.2	0.9	84.0	11	8
p,p'-DDT	0.6, 1.2	0.9	97.5	21	12
p,p'-DDE	0.2, 0.4	0.9	102	11	12
Mirex	0.6, 1.2	0.9	85.9	22	7
Pentachlorobenzene †	1.0	0.9	94	12	5
Pentachlorophenol	1.0	0.9	107	16	5
2,4,5-Trichlorophenol †	1.0	0.9	108	3	5
2,4-D Esters:					
isopropyl	0.5	3.6	92.0	5	12
butyl	0.5	3.6	82.0	10	11
isobutyl	0.5	3.6	79.0	20	12
isooctyl	0.5	3.6	>80*	--	--

* Not vaporized. Value base on %RE = 81.0 (RSD = 10%, n = 6).

† Semivolatile organochlorine pesticides.

TABLE 3. SAMPLING EFFICIENCIES FOR ORGANOPHOSPHORUS PESTICIDES

Compound	Quantity Introduced,[b] ug	Sampling Efficiency, % mean	RSD	n
Dichlorvos (DDVP)	0.2	72.0	13	2
Ronnel	0.2	106	8	12
Chlorpyrifos	0.2	108	9	12
Diazinon[a]	1.0	84.0	18	18
Methyl parathion[a]	0.6	80.0	19	18
Ethyl parathion[a]	0.3	75.9	15	18
Malathion[a]	0.3	100[c]	--	--

[a] Analyzed by gas chromatography with nitrogen phosphorus detector or flame photometric detector.

[b] Air volume = 0.9 m^3.

[c] Decomposed in generator; value based on %RE = 101 (RDS = 7, n = 4).

TABLE 4. EXTRACTION AND 24-HOUR SAMPLING EFFICIENCIES FOR VARIOUS PESTICIDES AND RELATED COMPOUNDS

Compound	Extraction Efficiency, *%		Sampling Efficiency, † %, at					
			10 ng/m^3		100 ng/m^3		1000 ng/m^3	
	mean	RSD	mean	RSD	mean	RSD	mean	RSD
Chlorpyrifos	83.3	11.5	83.7	18.0	92.7	15.1	83.7	18.0
Pentachlorophenol	84.0	22.6	66.7	42.2	52.3	36.2	66.7	42.2
Chlordane	95.0	7.1	96.0	1.4	74.0	8.5	96.0	1.4
Lindane	96.0	6.9	91.7	11.6	93.0	2.6	91.7	11.6
DDVP	88.3	20.2	51.0	53.7	106.0	1.4	51.0	53.7
2,4-D methyl ester	--	--	75.3	6.8	58.0	23.6	75.3	6.8
Heptachlor	99.0	1.7	97.3	13.6	103.0	17.3	97.3	13.6
Aldrin	97.7	4.0	90.7	5.5	94.0	2.6	90.7	5.5
Dieldrin	95.0	7.0	82.7	7.6	85.0	11.5	82.7	7.6
Ronnel	80.3	19.5	74.7	12.1	60.7	15.5	74.7	12.2
Diazinon	72.0	21.8	63.7	18.9	41.3	26.6	63.7	19.9
trans-Nonachlor	97.7	4.0	96.7	4.2	101.7	15.3	96.7	4.2
Oxychlordane	100.0	0.0	95.3	9.5	94.3	1.2	95.3	9.5
α-BHC	98.0	3.5	86.7	13.7	97.0	18.2	86.7	13.7
Chlorothalonil	90.3	8.4	76.7	6.1	70.3	6.5	76.7	6.1
Heptachlor epoxide	100.0	0.0	95.3	5.5	97.7	14.2	95.3	5.5

* Mean values for one spike at 550 ng/plug and two spikes at 5500 ng/plug.

† Mean values for three determinations.

Table 5. EXTRACTION AND 24-HOUR SAMPLING EFFICIENCIES FOR VARIOUS PESTICIDES AND RELATED COMPOUNDS

Compound	Extraction Efficiency, *%		Retention Efficiency, † %, at					
			10 ng/m^3		100 ng/m^3		1000 ng/m^3	
	mean	RSD	mean	RSD	mean	RSD	mean	RSD
Dicofol	57.0	8.5	38.0	25.9	65.0	8.7	69.0	--
Captan	73.0	12.7	56.0	--	45.5	64.3	84.3	16.3
Methoxychlor	65.5	4.9	--	--	--	--	78.5	2.1
Folpet	86.7	11.7	--	--	78.0	--	93.0	--

* Mean Values for one spike at 550 ng/plug and two spikes at 5500 ng/plug.

† Mean Values for generally three determinations.

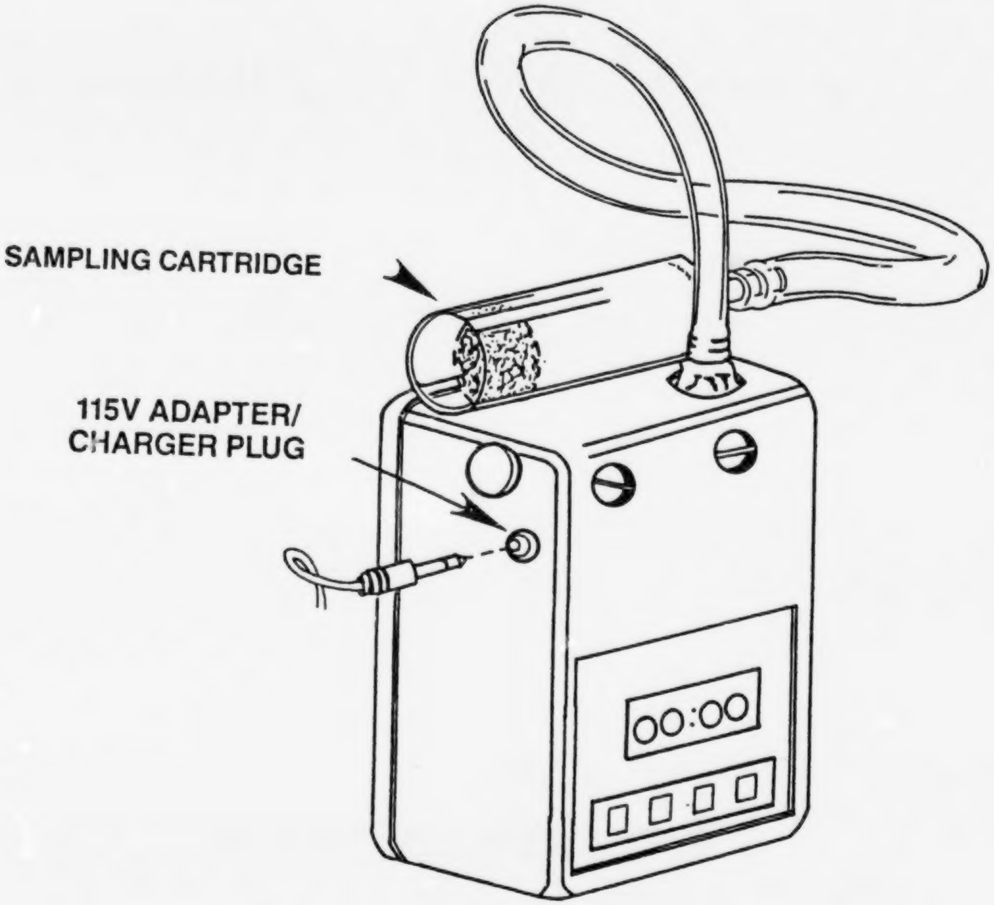

SAMPLING CARTRIDGE
115V ADAPTER/ CHARGER PLUG
00:00

FIGURE 1. LOW VOLUME AIR SAMPLER

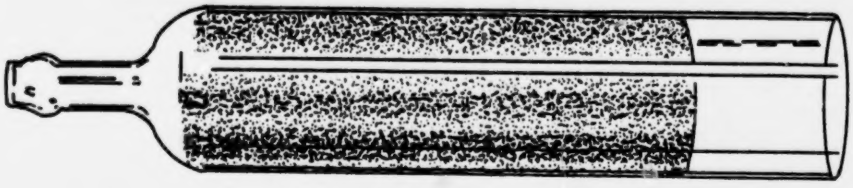


FIGURE 2. POLYURETHANE FOAM (PUF) SAMPLING CARTRIDGE

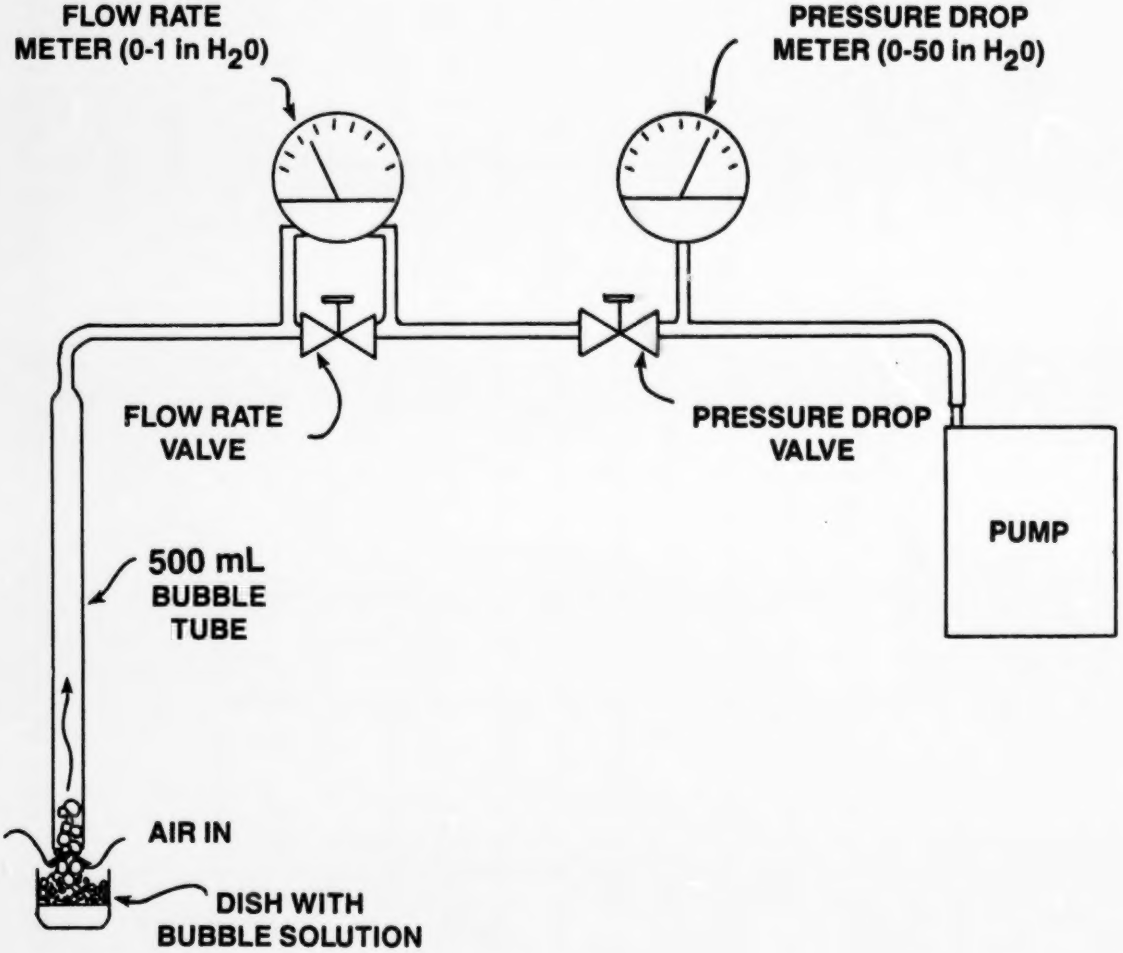

FLOW RATE
METER (0-1 in H_20)
PRESSURE DROP
METER (0-50 in H_20)
FLOW RATE
VALVE
PRESSURE DROP
VALVE
PUMP
500 mL
BUBBLE
TUBE
AIR IN
DISH WITH
BUBBLE SOLUTION

FIGURE 3. CALIBRATION ASSEMBLY FOR AIR SAMPLER PUMP

Site ______ Date ______ Performed by ______

Sampler S/N	Sampling Location I.D.	Height above Ground	PUF Cart. No.	Sampling Period		Sampling Time min.		Pump Timer hr. min.	Low flow Indication		Comments
				Start	Stop				Yes	No	

Checked by ______

Date ______

FIGURE 4. LOW VOLUME PESTICIDE SAMPLING DATA FORM

OPERATING CONDITIONS

Column Type: 1.5% SP 2250/1.95% SP 2401, ¼" glass.
Temperature: 200°C isothermal.
Detector: Electron Capture.
Carrier Gas: 5% Methane/95% Argon.
Flow Rate: 65 to 85 mL/min.

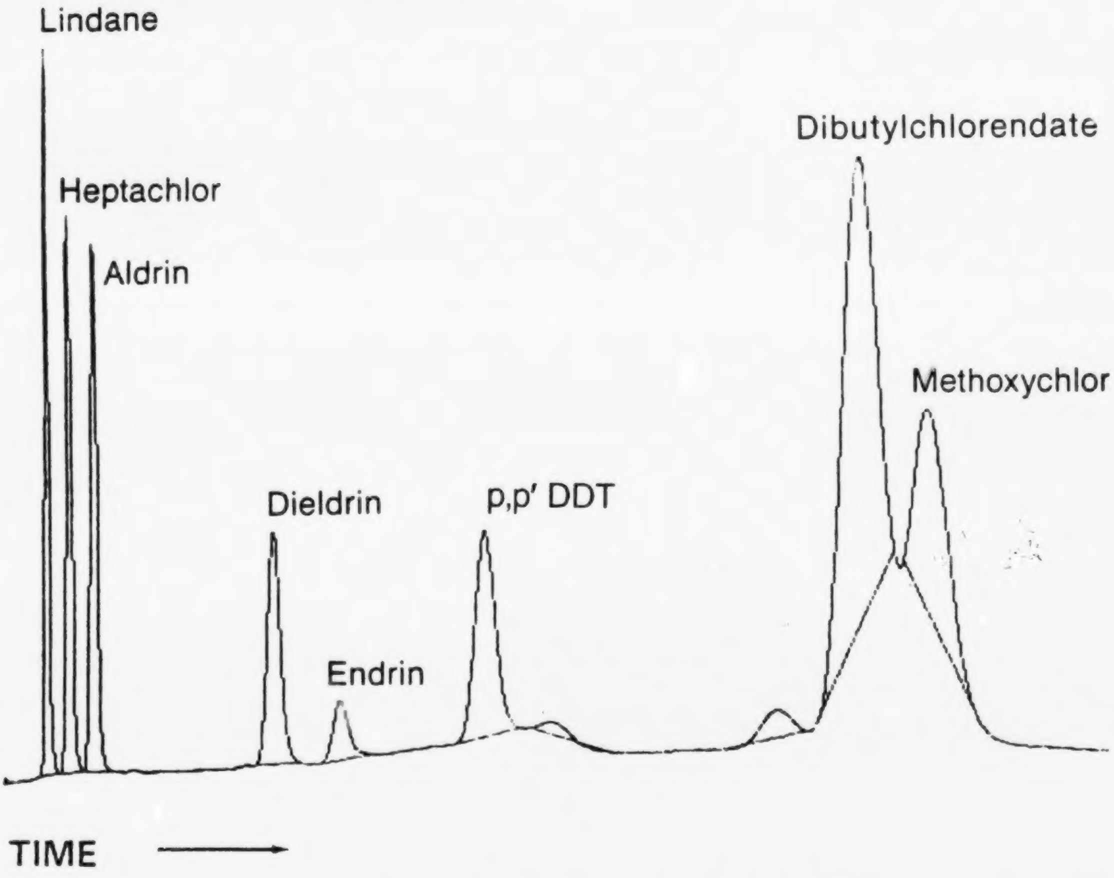


FIGURE 5. CHROMATOGRAM SHOWING A MIXTURE OF SINGLE COMPONENT PESTICIDES DETERMINED BY GC/ECD USING A PACKED COLUMN

EXTERNAL STANDARD TABLE
SINGLE COMPONENT PESTICIDE MIXTURE (5uL) ON
A PACKED COLUMN

RETENTION TIME	COMPOUND NAME	CONCENTRATION IN PG ON COLUMN	AREA/ HEIGHT
2.77	gamma-BHC (Lindane)	500	8.2
3.37	Heptachlor	500	10.4
4.03	Aldrin	500	12.0
8.90	Dieldrin	500	24.7
10.72	Endrin	500	30.2
14.63	p,p'-DDT	500	39.0
24.87	Dibutylchlorendate*	2500	61.4
26.82	Methoxychlor	2500	57.5

* Internal standard used for earlier pesticide detection.

FIGURE 6. CHROMATOGRAPHIC CHARACTERISTICS OF THE SINGLE COMPONENT PESTICIDE MIXTURE DETERMINED BY GC/ECD USING A PACKED COLUMN

OPERATING CONDITIONS

Column Type: DB-5 0.32 capillary, 0.25 um film thickness
Column Temperature Program: 90°C (4 min)/16°C per min to 154°C/4°C per min to 270°C.
Detector: Electron Capture
Carrier Gas: Helium at 1 mL/min.
Make Up Gas: 5% Methane/95% Argon at 60 mL/min.

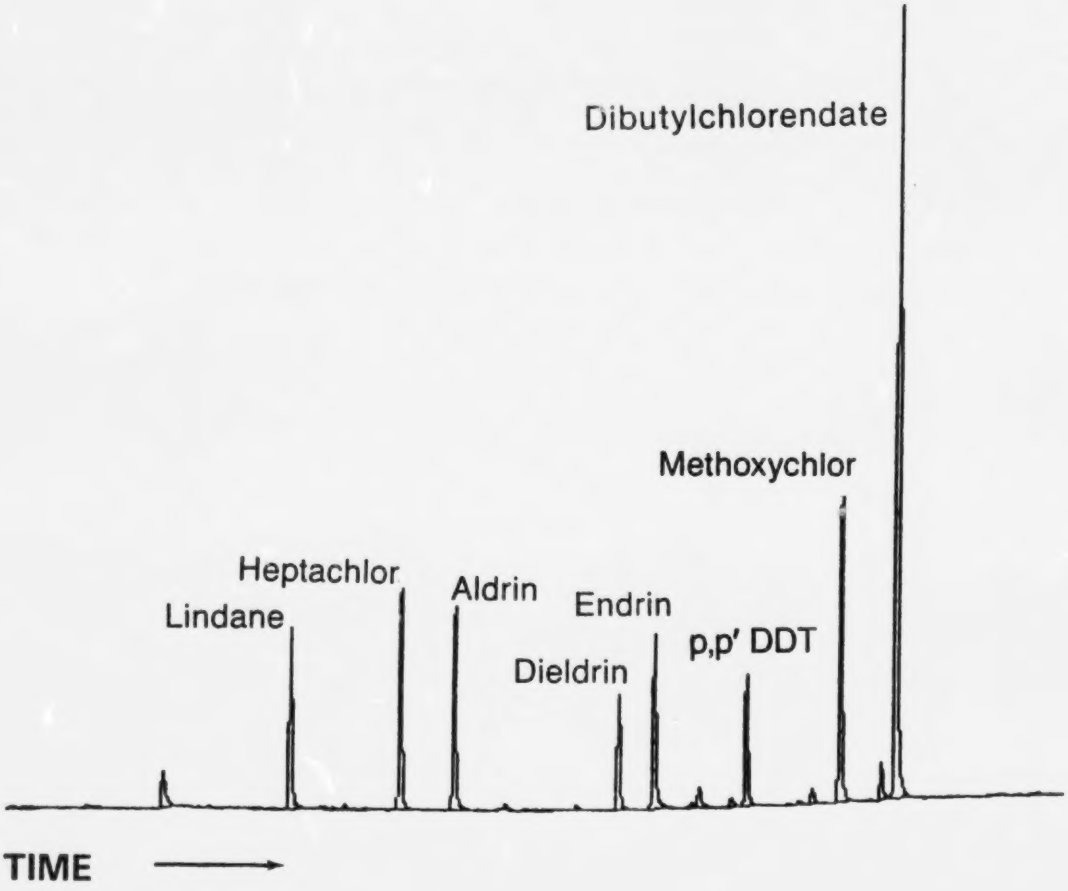


FIGURE 7. **CHROMATOGRAM SHOWING A MIXTURE OF SINGLE COMPONENT PESTICIDES DETERMINED BY GC/ECD USING A CAPILLARY COLUMN**

EXTERNAL STANDARD TABLE
SINGLE COMPONENT PESTICIDE MIXTURE (2uL) ON
ON A CAPILLARY COLUMN

RETENTION TIME	COMPOUND NAME	CONCENTRATION IN PG ON COLUMN	AREA/ HEIGHT
14.28	gamma-BHC (Lindane)	200	5.2
17.41	Heptachlor	200	5.3
18.96	Aldrin	200	5.4
23.63	Dieldrin	200	5.8
24.63	Endrin	200	6.3
27.24	p,p'-DDT	200	5.6
29.92	Methoxychlor	1000	5.5
31.49	Dibutylchlorendate*	1000	5.4

* Internal standard used for earlier pesticide detection.

FIGURE 8. CHROMATOGRAPHIC CHARACTERISTICS OF THE SINGLE COMPONENT PESTICIDE MIXTURE DETERMINED BY GC/ECD USING A CAPILLARY COLUMN

T010-37

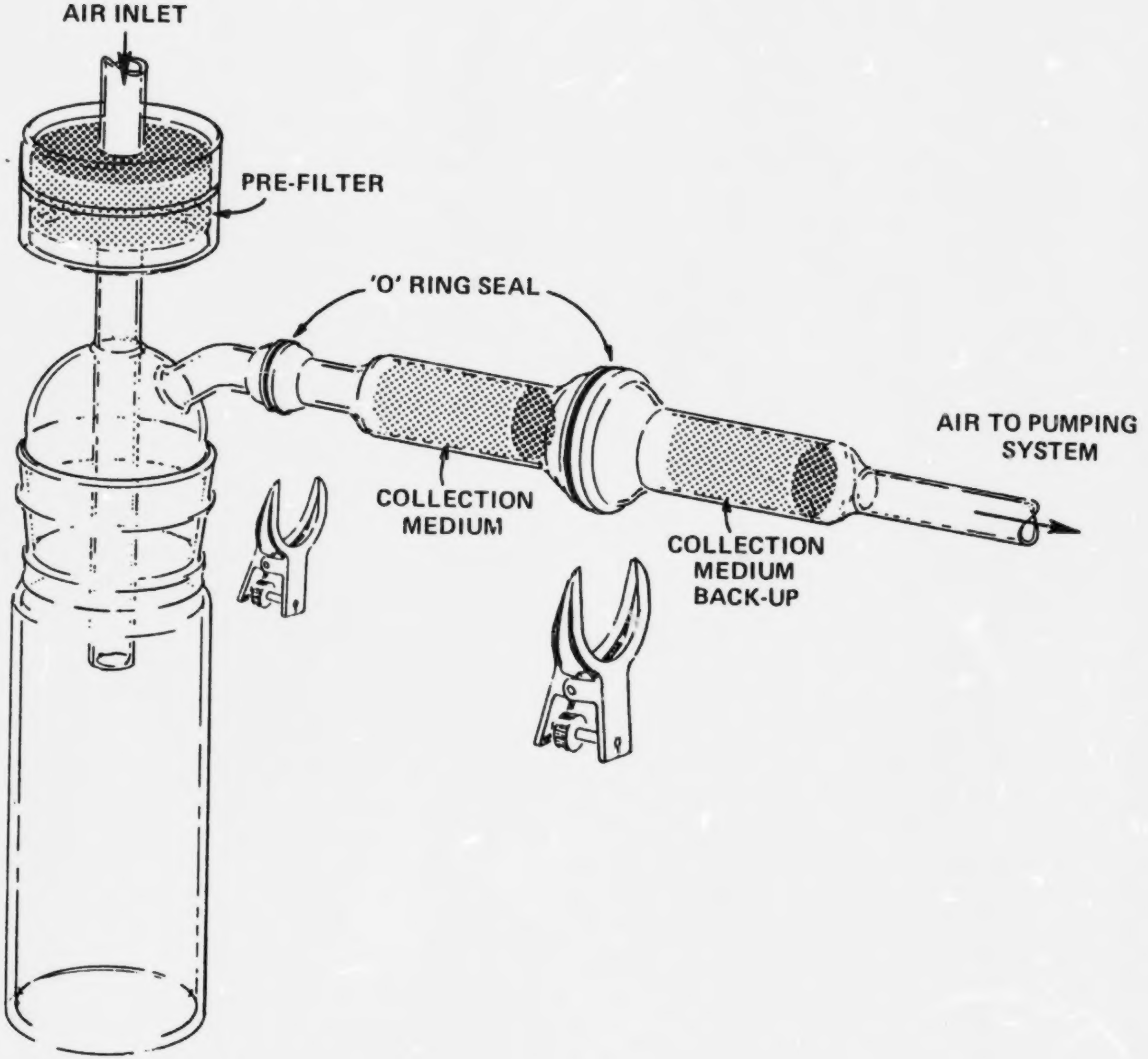

AIR INLET
PRE-FILTER
'O' RING SEAL
COLLECTION MEDIUM
COLLECTION MEDIUM BACK-UP
AIR TO PUMPING SYSTEM

FIGURE 9. APPARATUS FOR DETERMINING SAMPLING EFFICIENCIES

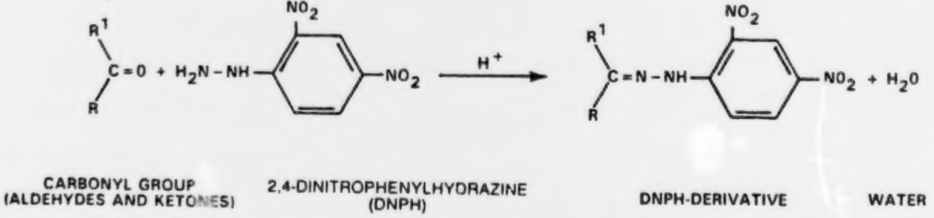
METHOD TO11-1

METHOD FOR THE DETERMINATION OF FORMALDEHYDE IN AMBIENT AIR USING ADSORBENT CARTRIDGE FOLLOWED BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

1. Scope

1.1 This document describes a method for the determination of formaldehyde in ambient air utilizing solid adsorbent followed by high performance liquid chromatographic detection. Formaldehyde has been found to be a major promoter in the formation of photochemical ozone. In particular, short term exposure to formaldehyde and other specific aldehydes (acetaldehyde, acrolein, crotonaldehyde) is known to cause irritation of the eyes, skin, and mucous membranes of the upper respiratory tract.

1.2 Compendium Method TO5, "Method For the Determination of Aldehydes and Ketones in Ambient Air Using High Performance Liquid Chromatography (HPLC)" involves drawing ambient air through a midget impinger sampling train containing 10 mL of 2N HCl/0.05% 2,4-dinitrophenylhydrazine (DNPH) reagent. Aldehydes and ketones readily form a stable derivative with the DNPH reagent, and the DNPH derivative is analyzed for aldehydes and ketones utilizing HPLC. Method TO11 modifies the sampling procedures outlined in Method TO5 by introducing a coated adsorbent for sampling formaldehyde. This current method is based on the specific reaction of organic carbonyl compounds (aldehydes and ketones) with DNPH-coated cartridges in the presence of an acid to form stable derivatives according to the following equation:



where R and R' are organic alkyl or aromatic group (ketones) or either substituent is a hydrogen (aldehydes).

The determination of formaldehyde from the DNPH-formaldehyde derivative is similar to Method TO5 in incorporating HPLC. The detection limits have been extended and other aldehydes and ketones can be determined as outlined in Section 14.

1.3 The sampling method gives a time-weighted average (TWA) sample. It can be used for long-term (1-24 hr) sampling of ambient air where the concentration of formaldehyde is generally in the low (1-20) ppb (v/v) or for short-term (5-60 min) sampling of source-impacted atmospheres where the concentration of formaldehyde could reach the ppm (v/v) levels.

1.4 The sampling flow rate, as described in this document, is presently limited to about 1.5 L/min. This limitation is principally due to the high pressure drop across the DNPH-coated silica gel cartridges. Because of this, the procedure is not compatible with pumps used in personal sampling equipments.

1.5 The method instructs the user to purchase Sep-PAK chromatographic grade silica gel cartridges (Waters Associates, 34 Maple St., Milford, MA 01757) and apply acidified DNPH in situ to each cartridge as part of the user-prepared quality assurance program (1,2). Commercially pre-coated DNPH cartridges are also available. [Caution: Recent studies have indicated abnormally high formaldehyde background levels in commercially prepacked cartridges. It is advised that three cartridges randomly selected from each production lot, be analyzed for formaldehyde prior to use to determine acceptable levels.] Thermosorb/F cartridges (Thermedics, Inc., 470 Wildwood St., P.O. Box 2999, Woburn, MA, 01888-1799) can be purchased prepacked. The cartridges are 1.5 cm ID x 2 cm long polyethylene tubes with Luer®-type fittings on each end. The adsorbent is composed of 60/80-mesh Florisil (magnesium silicate) coated with 2,4-dinitrophenylhydrazine. The adsorbent is held in place with 100 mesh stainless steel screens at each end. The precoated cartridges are used as received and are discarded after use. The cartridges are stored in glass culture tubes with polypropylene caps and placed in cold storage when not in use.

1.6 This method may involve hazardous materials, operations, and equipments. This method does not purport to address all the safety problems associated with its use. It is the responsibility of whoever uses this method to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. Applicable Documents

2.1 ASTM Standards

D1356 - Definition of Terms Relating to Atmospheric Sampling and Analysis

E682 - Practice for Liquid Chromatography Terms and Relationships

2.2 Other Documents

Existing Procedures (3-5)

Ambient Air Studies (6-8)

U. S. EPA Technical Assistance Document (9)

Indoor Air Studies (10-11)

3. Summary of Method

3.1 A known volume of ambient air is drawn through a prepacked silica gel cartridge coated with acidified DNPH at a sampling rate of 500-1200 mL/min for an appropriate period of time. Sampling rate and time are dependent upon carbonyl concentration in the test atmosphere.

3.2 After sampling, the sample cartridges are capped and placed in borosilicate glass culture tubes with polypropylene caps. The capped tubes are then placed in a friction-top can containing a pouch of charcoal and returned to the laboratory for analysis. Alternatively, the sample vials can be placed in a styrofoam box with appropriate padding for shipment to the laboratory. The cartridges may either be placed in cold storage until analysis or immediately washed by gravity feed elution of 6 mL of acetonitrile from a plastic syringe reservoir to a graduated test tube or a 5 mL volumetric flask.

3.3 The eluate is then topped to a known volume and refrigerated until analysis.

3.4 The DNPH-formaldehyde derivative is determined using isocratic reverse phase HPLC with an ultraviolet (UV) absorption detector operated at 360 nm.

3.5 A cartridge blank is likewise desorbed and analyzed as per Section 3.4.

3.6 Formaldehyde and other carbonyl compounds in the sample are identified and quantified by comparison of their retention times and peak heights or peak areas with those of standard solutions.

4. Significance

4.1 Formaldehyde has been found to be a major promoter in the formation of photochemical ozone (12). In particular, short term exposure to formaldehyde and other specific aldehydes (acetaldehyde, acrolein, crotonaldehyde) is known to cause irritation of the eyes, skin, and mucous membranes of the upper respiratory tract (13). Animal studies indicate that high concentrations can injure the lungs and other organs of the body (14). Formaldehyde may contribute to eye irritation and unpleasant odors that are common annoyances in polluted atmospheres.

4.2 Formaldehyde emissions result from incomplete combustion of hydrocarbons and other organic materials. The major emission sources appear to be vehicle exhaust, incineration of wastes, and burning of fuels (natural gas, fuel oil, and coal). In addition, significant amounts of atmospheric formaldehyde can result from photochemical reactions between reactive hydrocarbons and nitrogen oxides. Moreover, formaldehyde can react photochemically to produce other products, including ozone, peroxides, and peroxyacetyl nitrate compounds. Local sources of formaldehyde may include manufacturing and other industrial processes using the chemical. In particular, formaldehyde emissions are associated with any industrial process that results in the pyrolysis of organic compounds in air or oxygen. This test method provides a means to determine concentrations of formaldehyde and other carbonyl compounds in emissions sources in various working environment and in ambient indoor and outdoor atmospheres.

5. Definitions

5.1 Definitions used in this document and in any user-prepared Standard Operating Procedures (SOPs) should be consistent with ASTM Methods D1356 and E682. All abbreviations and symbols within this document are defined the first time they are used.

6. Interferences

6.1 This procedure has been written specifically for the sampling and analysis of formaldehyde. Interferences in the method are certain isomeric aldehydes or ketones that may be unresolved by the HPLC system when analyzing for other aldehydes and ketones. Organic compounds that have the same retention time and significant absorbance at 360 nm as the DNPH derivative of formaldehyde will interfere. Such interferences can often be overcome by altering the separation conditions (e.g., using alternative HPLC columns or mobile phase compositions). However, other aldehydes and ketones can be detected with a modification of the basic procedure. In particular, chromatographic conditions can be optimized to separate acrolein, acetone, and propionaldehyde and the following higher molecular weight aldehydes and ketones (within an analysis time of about one hour) by utilizing two Zorbax ODS columns in series under a linear gradient program:

Formaldehyde
Acetaldehyde
Acrolein
Acetone
Propionaldehyde
Crotonaldehyde
Butyraldehyde
Benzaldehyde
Isovaleraldehyde
Valeraldehyde
o-Tolualdehyde
m-Tolualdehyde
p-Tolualdehyde
Hexanaldehyde
2,5-Dimethylbenzaldehyde

The linear gradient program varies the mobile phase composition periodically to achieve maximum resolution of the C-3, C-4, and benzaldehyde region of the chromatogram. The following gradient program was found to be adequate to achieve this goal: Upon sample injection, linear gradient from 60-75% acetonitrile/40-25% water in 30 minutes, linear gradient from 75-100% acetonitrile/25-0% water in 20 minutes, hold at 100% acetonitrile for 5 minutes, reverse gradient to 60% acetonitrile/40% water in 1 minute, and maintain isocratic at 60% acetonitrile/40% water for 15 minutes.

6.2 Formaldehyde contamination of the DNPH reagent is a frequently encountered problem. The DNPH must be purified by multiple recrystallizations in UV grade acetonitrile. Recrystallization is accomplished at 40-60°C by slow evaporation of the solvent to maximize crystal size. The purified DNPH crystals are stored under UV grade acetonitrile until use. Impurity levels of carbonyl compounds in the DNPH are determined by HPLC prior to use and should be less than 0.025 ug/mL.

7. Apparatus

7.1 Isocratic HPLC system consisting of a mobile phase reservoir; a high pressure pump; an injection valve (automatic sampler with an optional 25-uL loop injector); a Zorbax ODS (DuPont Instruments, Wilmington, DE), or equivalent C-18, reverse phase (RP) column, or equivalent (25 cm x 4.6 mm ID); a variable wavelength UV detector operating at 360 nm; and a data system or strip chart recorder (Figure 1).

7.2 Sampling system - capable of accurately and precisely sampling 100-1500 mL/min of ambient air (Figure 2). The dry test meter may not be accurate at flows below 500 mL/min, and should then be replaced by recorded flow readings at the start, finish, and hourly during the collection. The sample pump consists of a diaphragm or metal bellows pump capable of extracting an air sample between 500-1200 mL/min. [Note: A normal pressure drop through the sample cartridge approaches 14 cm Hg at a sampling rate of 1.5 L/min.]

7.3 Stopwatch.

7.4 Friction-top metal can (e.g., 1-gallon paint can) or a styrofoam box with polyethlyene-air bubble padding - to hold sample vials.

7.5 Thermometer - to record ambient temperature.

7.6 Barometer (optional).

7.7 Suction filtration apparatus - for filtering HPLC mobile phase.

7.8 Volumetric flasks - various sizes, 5-2000 mL.

7.9 Pipets - various sizes, 1-50 mL.

7.10 Helium purge line (optional) - for degassing HPLC mobile phase.

7.11 Erlenmeyer flask, 1 L - for preparing HPLC mobile phase.

7.12 Graduated cylinder, 1 L - for preparing HPLC mobile phase.

7.13 Syringe, 100-250 uL - for HPLC injection.

7.14 Sample vials.

7.15 Melting point apparatus.

7.16 Rotameters.

7.17 Calibrated syringes.

7.18 Special glass apparatus for rinsing, storing and dispensing saturated DNPH stock reagent (Figure 3).

7.19 Mass flow meters and mass flow controllers for metering/setting air flow rate through sample cartridge of 500-1200 mL/min. [Note: The mass flow controllers are necessary because cartridges have a high pressure drop and at maximum flow rates, the cartridge behaves like a "critical orifice." Recent studies have shown that critical flow orifices may be used for 24-hour sampling periods at a maximum rate of 1 L/min for atmospheres not heavily loaded with particulates without any problems.]

7.20 Positive displacement, repetitive dispensing pipets (Lab-Industries, or equivalent), 0-10 mL range.

7.21 Cartridge drying manifold with multiple standard male Luer® connectors.

7.22 Liquid syringes, 10 mL (polypropylene syringes are adequate) for preparing DNPH-coated cartridges.

7.23 Syringe rack - made of an aluminum plate (0.16 x 36 x 53 cm) with adjustable legs on four corners. A matrix (5 x 9) of circular holes of diameter slightly larger than the diameter of the 10-mL syringes was symetrically drilled from the center of the plate to enable batch processing of 45 cartridges for cleaning, coating, and/or sample elution.

7.24 Luer® fittings/plugs - to connect cartridges to sampling system and to cap prepared cartridges.

7.25 Hot plates, beakers, flasks, measuring and disposable pipets, volumetric flasks, etc. - used in the purification of DNPH.

7.26 Borosilicate glass culture tubes (20 mm x 125 mm) with polypropylene screw caps - used to transport Sep-PAK coated cartridges for field applications (Fisher Scientific, Pittsburgh, PA, or equivalent).

7.27 Heated probe - necessary when ambient temperature to be sampled is below 60°F to insure the effective collection of formaldehyde as a hydrazone.

7.28 Cartridge sampler - prepacked silica gel cartridge, Sep-PAK (Waters Associates, Milford, MA 01757, or equivalent) coated in situ with DNPH according to Section 9.

7.29 Polyethylene gloves - used to handle Sep-PAK silica gel cartridges, best source.

8. Reagents and Materials

8.1 2,4-Dinitrophenylhydrazine (DNPH)- Aldrich Chemical or J.T. Baker, reagent grade or equivalent. Recrystallize at least twice with UV grade acetonitrile before use.

8.2 Acetonitrile - UV grade, Burdick and Jackson "distilled-in-glass," or equivalent.

8.3 Deionized-distilled water - charcoal filtered.

8.4 Perchloric acid - analytical grade, best source.

8.5 Hydrochloric acid - analytical grade, best source.

8.6 Formaldehyde - analytical grade, best source.

8.7 Aldehydes and ketones, analytical grade, best source - used for preparation of DNPH derivative standards (optional).

8.8 Ethanol or methanol - analytical grade, best source.

8.9 Sep-PAK silica gel cartridge - Waters Associates, 34 Maple St., Milford, MA, 01757, or equivalent.

8.10 Nitrogen - high purity grade, best source.

8.11 Charcoal - granular, best source.

8.12 Helium - high purity grade, best source.

9. Preparation of Reagents and Cartridges

9.1 Purification of 2,4-Dinitrophenylhydrazine (DNPH)

[Note: This procedure should be performed under a properly ventilated hood.]

9.1.1 Prepare a supersaturated solution of DNPH by boiling excess DNPH in 200 mL of acetonitrile for approximately one hour.

9.1.2 After one hour, remove and transfer the supernatant to a covered beaker on a hot plate and allow gradual cooling to 40-60°C.

9.1.3 Maintain the solution at this temperature (40-60°C) until 95% of solvent has evaporated.

9.1.4 Decant solution to waste, and rinse crystals twice with three times their apparent volume of acetonitrile. [Note: Various health effects are resultant from the inhalation of acetonitrile. At 500 ppm in air, brief inhalation has produced nose and throat irritation. At 160 ppm, inhalation for 4 hours has caused flushing of the face (2 hour delay after exposure) and bronchial tightness (5 hour delay). Heavier exposures have produced systemic effects with symptoms ranging from headache, nausea, and lassitude to vomiting, chest or abdominal pain, respiratory depression, extreme weakness, stupor, convulsions and death (dependent upon concentration and time).]

9.1.5 Transfer crystals to another clean beaker, add 200 mL of acetonitrile, heat to boiling, and again let crystals grow slowly at 40-60°C until 95% of the solvent has evaporated.

9.1.6 Repeat rinsing process as described in Section 9.1.4.

9.1.7 Take an aliquot of the second rinse, dilute 10 times with acetonitrile, acidify with 1 mL of 3.8 M perchloric acid per 100 mL of DNPH solution, and analyze by HPLC.

9.1.8 The chromatogram illustrated in Figure 4 represents an acceptable impurity level of <0.025 ug/mL of formaldehyde in recrystallized DNPH reagent. An acceptable impurity level for an intended sampling application may be defined as the mass of the analyte (e.g. DNPH-formaldehyde derivative) in a unit volume of the reagent solution equivalent to less than one tenth (0.1) the mass of the corresponding analyte from a volume of an air sample when the carbonyl (e.g. formaldehyde) is collected as DNPH derivative in an equal unit volume of the reagent solution. An impurity level unacceptable for a typical 10 L sample volume may be acceptable if sample volume is increased to 100 L. The impurity level of DNPH should be below the sensitivity (ppb, v/v) level indicated in Table 1 for the anticipated sample volume. If the impurity level is not acceptable for intended sampling application, repeat recrystallization. A special glass apparatus should be used for the final rinse and storage according to the following procedure:

9.1.8.1 Transfer the crystals to the special glass apparatus (Figure 3).

9.1.8.2 Add about 25 mL of acetonitrile, agitate gently, and let solution equilibrate for 10 minutes.

9.1.8.3 Drain the solution by properly positioning the three-way stopcock. [Note: The purified crystals should not be allowed to contact laboratory air except for a brief moment. This is accomplished by using the DNPH-coated silica cartridge on the gas inlet of the special glass apparatus.]

9.1.8.4 After draining, turn stopcock so drain tube is connected to measuring reservoir.

9.1.8.5 Introduce acetonitrile through measuring reservoir.

9.1.8.6 Rinsing should be repeated with 20-mL portions of acetonitrile until a satisfactorily low impurity level in the supernatant is confirmed by HPLC analysis. An impurity level of <0.025 ug/mL formaldehyde should be achieved, as illustrated in Figure 4.

9.1.9 If special glass apparatus is not available, transfer the purified crystals to an all-glass reagent bottle, add 200 mL of acetonitrile, stopper, shake gently, and let stand overnight. Analyze supernatant by HPLC according to Section 11. The impurity level should be comparable to that shown in Figure 4.

9.1.10 If the impurity level is not satisfactory, pipet off the solution to waste, then add 25 mL of acetonitrile to the purified crystals. Repeat Section 9.1.8.6.

9.1.11 If the impurity level is satisfactory, add another 25 mL of acetonitrile, stopper and shake the reagent bottle, then set aside. The saturated solution above the purified crystals is the stock DNPH reagent.

9.1.12 After purification, purity of the DNPH reagent can be maintained by storing in the special glass apparatus.

9.1.13 Maintain only a minimum volume of saturated solution adequate for day to day operation. This will minimize wastage of purified reagent should it ever become necessary to re-rinse the crystals to decrease the level of impurity for applications requiring more stringent purity specifications.

9.1.14 Use clean pipets when removing saturated DNPH stock solution for any analytical applications. Do not pour the stock solution from the reagent bottle.

9.2 Preparation of DNPH-Formaldehyde Derivative

9.2.1 Titrate a saturated solution of DNPH in 2N HCl with formaldehyde (other aldehydes or ketones may be used if their detection is desirable).

9.2.2 Filter the colored precipitate, wash with 2N HCl and water and let precipitate air dry.

9.2.3 Check the purity of the DNPH-formaldehyde derivative by melting point determination table or HPLC analysis. If the impurity level is not acceptable, recrystallize the derivative in ethanol. Repeat purity check and recrystallization as necessary until acceptable level of purity (e.g. 99%) is achieved.

9.3 Preparation of DNPH-Formaldehyde Standards

9.3.1 Prepare a standard stock solution of the DNPH-formaldehyde derivative by dissolving accurately weighed amounts in acetonitrile.

9.3.2 Prepare a working calibration standard mix from the standard stock solution. The concentration of the DNPH-formaldehyde compound in the standard mix solutions should be adjusted to reflect relative distribution in a real sample. [Note: Individual stock solutions of approximately 100 mg/L are prepared by dissolving 10 mg of the solid derivative in 100 mL of acetonitrile. The individual solution is used to prepare calibration standards containing the derivative of interest at concentrations of 0.5-20 ug/L, which spans the concentration of interest for most ambient air work.]

9.3.3 Store all standard solutions in a refrigerator. They should be stable for several months.

9.4 Preparation of DNPH-Coated Sep-PAK Cartridges

[Note: This procedure must be performed in an atmosphere with a very low aldehyde background. All glassware and plastic ware must be scrupulously cleaned and rinsed with deionized water and aldehyde free acetonitrile. Contact of reagents with laboratory air must be minimized. Polyethylene gloves must be worn when handling the cartridges.]

9.4.1 DNPH Coating Solution

9.4.1.1 Pipet 30 mL of saturated DNPH stock solution to a 1000 mL volumetric flask then add 500 mL acetonitrile.

9.4.1.2 Acidify with 1.0 mL of concentrated HCl. [Note: The atmosphere above the acidified solution should preferably be filtered through a DNPH-coated silica gel cartridge to minimize contamination from laboratory air.] Shake solution then make up to volume with acetonitrile. Stopper the flask, invert and shake several times until the solution is homogeneous. Transfer the acidified solution to a reagent bottle with a 0-10 mL range positive displacement dispenser.

9.4.1.3 Prime the dispenser and slowly dispense 10-20 mL to waste.

9.4.1.4 Dispense an aliquot solution to a sample vial, and check the impurity level of the acidified solution by HPLC according to Section 9.1 and illustrated in Figure 4.

9.4.1.5 The impurity level should be <0.025 ug/mL formaldehyde similar to that in the DNPH coating solution.

9.4.2 Coating of Sep-PAK Cartridges

9.4.2.1 Open the Sep-PAK package, connect the short end to a 10-mL syringe, and place it in the syringe rack. [Note: Prepare as many cartridges and syringes as possible.]

9.4.2.2 Using a positive displacement repetitive pipet, add 10 mL of acetonitrile to each of the syringes.

9.4.2.3 Let liquid drain to waste by gravity. [Note: Remove any air bubbles that may be trapped between the syringe and the silica cartridge by displacing them with the acetonitrile in the syringe.]

9.4.2.4 Set the repetitive dispenser containing the acidified DNPH coating solution to dispense 7 mL into the cartridges.

9.4.2.5 Once the effluent flow at the outlet of the cartridge has stopped, dispense 7 mL of the coating reagent into each of the syringes.

9.4.2.6 Let the coating reagent drain by gravity through the cartridge until flow at the other end of the cartridge stops.

9.4.2.7 Wipe the excess liquid at the outlet of each of the cartridges with clean tissue paper.

9.4.2.8 Assemble a drying manifold with a scrubber or "guard cartridge" connected to each of the exit ports. These "guard cartridges" are DNPH-coated and serve to remove any trace of formaldehyde in the nitrogen gas supply.

9.4.2.9 Remove the cartridges from the syringes and connect the short ends to the exit end of the scrubber cartridge.

9.4.2.10 Pass nitrogen through each of the cartridges at about 300-400 mL/min for 5-10 minutes.

9.4.2.11 Within 10 minutes of the drying process, rinse the exterior surfaces and outlet ends of the cartridges with acetonitrile using a Pasteur pipet.

9.4.2.12 Stop the flow of nitrogen after 15 minutes and insert cartridge connectors (flared at both ends 0.25 OD x 1 in Teflon FEP tubing with ID slightly smaller than the OD of the cartridge port) to the long end of the scrubber cartridges.

9.4.2.13 Connect the short ends of a batch of the coated cartridges to the scrubbers and pass nitrogen at about 300-400 mL/min.

9.4.2.14 Follow procedure in Section 9.4.2.11.

9.4.2.15 After 15 minutes, stop the flow of nitrogen, remove the dried cartridges and wipe the cartridge exterior free of rinse acetonitrile.

9.4.2.16 Plug both ends of the coated cartridge with standard polypropylene Luer® male plugs, place the plugged cartridge in a borosilicate glass culture tube with polypropylene screw caps.

9.4.2.17 Put a serial number and a lot number label on each of the individual cartridge glass storage container and store the prepared lot in the refrigerator until use.

9.4.2.18 Store cartridges in an all-glass stoppered reagent bottle in a refrigerator until use. [Note: Plugged cartridges could also be placed in screw-capped glass culture tubes and placed in a refrigerator until use.] Cartridges will maintain their integrity for up to 90 days stored in refrigerated, capped culture tubes.

9.4.2.19 Before transport, remove the glass-stoppered reagent bottles (or screw-capped glass culture tubes) containing the adsorbent tubes from the refrigerator and place the tubes individually in labeled glass culture tubes. Place culture tubes in a friction-top metal can containing 1-2 inches of charcoal for shipment to sampling location.

9.4.2.20 As an alternative to friction-top cans for transporting sample cartridges, the coated cartridges could be shipped in their individual glass containers. A big batch of coated cartridges in individual glass containers may be packed in a styrofoam box for shipment to the field. The box should be padded with clean tissue paper or polyethylene-air bubble padding. Do not use polyurethane foam or newspaper as padding material.

9.4.2.21 The cartridges should be immediately stored in a refrigerator upon arrival in the field.

10. Sampling

10.1 The sampling system is assembled and should be similar to that shown in Figure 2. [Note: Figure 2(a) illustrates a three tube/one pump configuration. The tester should ensure that the pump is capable of constant flow rate throughout the sampling period.] The coated cartridges can be used as direct probes and traps for sampling ambient air when the temperature is above freezing. [Note: For sampling ambient air below freezing, a short length (30-60 cm) of heated (50-60°C) stainless steel tubing must be added to condition the air sample prior to collection on adsorbent tubes.] Two types of sampling systems are shown in Figure 2. For purposes of discussion, the following procedure assumes the use of a dry test meter. [Note: The dry test meter may not be accurate at flows below 500 mL/min and should be backed up by recorded flow readings at the start, finish, and hourly intervals during sample collection.]

10.2 Before sample collection, the system is checked for leaks. Plug the input end of the cartridge so no flow is indicated at the output end of the pump. The mass flow meter should not indicate any air flow through the sampling apparatus.

10.3 The entire assembly (including a "dummy" sampling cartridge) is installed and the flow rate checked at a value near the desired rate. In general, flow rates of 500-1200 mL/min should be employed. The total moles of carbonyl in the volume of air sampled should not exceed that of the DNPH concentration (2 mg/cartridge). In general, a safe estimate of the sample size should be 75% of the DNPH loading of the cartridge. Generally, calibration is accomplished using a soap bubble flow meter or calibrated wet test meter connected to the flow exit, assuming the system is sealed. [Note: ASTM Method 3686 describes an appropriate calibration scheme that does not require a sealed flow system downstream of the pump.]

10.4 Ideally, a dry gas meter is included in the system to record total flow. If a dry gas meter is not available, the operator must measure and record the sampling flow rate at the beginning and end of the sampling period to determine sample volume. If the sampling period exceeds two hours, the flow rate should be measured at intermediate points during the sampling period. Ideally, a rotameter should be included to allow observation of the flow rate without interruption of the sampling process.

10.5 Before sampling, remove the glass culture tube from the friction-top metal can or styrofoam box. Let the cartridge warm to ambient temperature in the glass tube before connecting it to the sample train.

10.6 Using polyethylene gloves, remove the coated cartridge from the glass tube and connect it to the sampling system with a Luer® adapter fitting. Seal the glass tube for later use, and connect the cartridge to the sampling train so that its short end becomes the sample inlet. Record the following parameters on the sampling data sheet (Figure 5): date, sampling location, time, ambient temperature, barometric pressure (if available), relative humidity (if available), dry gas meter reading (if appropriate), flow rate, rotameter setting, cartridge batch number, and dry gas meter pump identification numbers.

10.7 The sampler is turned on and the flow is adjusted to the desired rate. A typical flow rate through one cartridge is 1.0 L/min and 0.8 L/min for two tandem cartridges.

10.8 The sampler is operated for the desired period, with periodic recording of the variables listed above.

10.9 At the end of the sampling period, the parameters listed in Section 10.6 are recorded and the sample flow is stopped. If a dry gas meter is not used, the flow rate must be checked at the end of the sampling interval. If the flow rates at the beginning and end of the sampling period differ by more than 15%, the sample should be marked as suspect.

10.10 Immediately after sampling, remove the cartridge (using polyethylene gloves) from the sampling system, cap with Luer® end plugs, and place it back in the original labeled glass culture tube. Cap the culture tube, seal it with Teflon® tape, and place it in a friction-top can containing 1-2 inches of granular charcoal or styrofoam box with appropriate padding. Refrigerate the the culture tubes until analysis. Refrigeration period prior to analysis should not exceed 30 days. [Note: If samples are to be shipped to a central laboratory for analysis, the duration of the non-refrigerated period should be kept to a minimum, preferably less than two days.]

10.11 If a dry gas meter or equivalent total flow indicator is not used, the average sample flow rate must be calculated according to the following equation:

$$Q_A = \frac{Q_1 + Q_2 + \ldots Q_N}{N}$$

where:

Q_A = average flow rate (mL/min).

$Q_1, Q_2, \ldots Q_N$ = flow rates determined at beginning, end, and intermediate points during sampling.

N = number of points averaged.

10.12 The total flow rate is then calculated using the following equation:

$$V_m = \frac{(T_2 - T_1) \times Q_A}{1000}$$

where:

V_m = total volume (L) sampled at measured temperature and pressure.

T_2 = stop time (minutes).

T_1 = start time (minutes).

$T_2 - T_1$ = total sampling time (minutes).

Q_A = average flow rate (mL/min).

10.13 The total volume (V_s) at standard conditions, 25°C and 760 mm Hg, is calculated from the following equation:

$$V_s = V_m \times \frac{\overline{P}_A}{760} \times \frac{298}{273 + \overline{t}_A}$$

where:

V_s = total sample volume (L) at 25°C and 760 mm Hg pressure.

V_m = total sample volume (L) at measured temperature and pressure.

$\overline{P}_A$ = average ambient pressure (mm Hg).

$\overline{t}_A$ = average ambient temperature (°C).

11. Sample Analysis

11.1 Sample Preparation

11.1.1 The samples are returned to the laboratory in a friction-top can containing 1-2 inches of granular charcoal and stored in a refrigerator until analysis. Alternatively, the samples may also be stored alone in their individual glass containers. The time between sampling and analysis should not exceed 30 days.

11.2 Sample Desorption

11.2.1 Remove the sample cartridge form the labeled culture tube. Connect the sample cartridge (outlet end during sampling) to a clean syringe. [Note: The liquid flow during desorption should be in the reverse direction of air flow during sample collection.]

11.2.2 Place the cartridge/syringe in the syringe rack.

11.2.3 Backflush the cartridge (gravity feed) by passing 6 mL of acetonitrile from the syringe through the cartridge to a graduated test tube or to a 5-mL volumetric flask. [Note: A dry cartridge has an acetonitrile holdup volume slightly greater than 1 mL. The eluate flow may stop before the acetonitrile in the syringe is completely drained into the cartridge because of air trapped between the cartridge filter and the syringe Luer® tip. If this happens, displace the trapped air with the acetronitrile in the syringe using a long-tip disposable Pasteur pipet.]

11.2.4 Dilute to the 5-mL mark with acetonitrile. Label the flask with sample identification. Pipet two aliquots into sample vials with Teflon-lined septa. Analyze the first aliquot for the derivative carbonyls by HPLC. Store the second aliquot in the refrigerator until sample analysis.

11.3 HPLC Analysis

11.3.1 The HPLC system is assembled and calibrated as described in Section 11.4. The operating parameters are as follows:

Column: Zorbax ODS (4.6 mm ID x 25 cm), or equivalent.
Mobile Phase: 60% acetonitrile/40% water, isocratic.
Detector: ultraviolet, operating at 360 nm.
Flow Rate: 1.0 mL/min.
Retention Time: 7 minutes for formaldehyde with one Zorbax ODS column.
13 minutes for formaldehyde with two Zorbax ODS columns.
Sample Injection Volume: 25 uL.

Before each analysis, the detector baseline is checked to ensure stable conditions.

11.3.2 The HPLC mobile phase is prepared by mixing 600 mL of acetonitrile and 400 mL of water. This mixture is filtered through a 0.22-um polyester membrane filter in an all-glass and Teflon® suction filtration apparatus. The filtered mobile phase is degassed by purging with helium for 10-15 minutes (100 mL/min) or by heating to 60°C for 5-10 minutes in an Erlenmeyer flask covered with a watch glass. A constant back pressure restrictor (350 kPa) or short length (15-30 cm) of 0.25 mm (0.01 inch) ID Teflon® tubing should be placed after the detector to eliminate further mobile phase outgassing.

11.3.3 The mobile phase is placed in the HPLC solvent reservoir and the pump is set at a flow rate of 1.0 mL/min and allowed to pump for 20-30 minutes before the first analysis. The detector is switched on at least 30 minutes before the first analysis, and the detector output is displayed on a strip chart recorder or similar output device.

11.3.4 A 100-uL aliquot of the sample is drawn into a clean HPLC injection syringe. The sample injection loop (25 uL) is loaded and an injection is made. The data system, if available, is activated simultaneously with the injection, and the point of injection is marked on the strip chart recorder.

11.3.5 After approximately one minute, the injection valve is returned to the "inject" position and the syringe and valve are rinsed or flushed with acetonitrile/water mixture in preparation for the next sample analysis. [Note: The flush/rinse solvent should not pass through the sample loop during flushing.] The loop is clean while the valve is in the "inject" mode.

11.3.6 After elution of the DNPH-formaldehyde derivative (Figure 6), data acquisition is terminated and the component concentrations are calculated as described in Section 12.

11.3.7 After a stable baseline is achieved, the system can be used for further sample analyses as described above. [Note: After several cartridge analyses, buildup on the column may be removed by flushing with several column volumes of 100% acetonitrile.]

11.3.8 If the concentration of analyte exceeds the linear range of the instrument, the sample should be diluted with mobile phase, or a smaller volume can be injected into the HPLC.

11.3.9 If the retention time is not duplicated (±10%), as determined by the calibration curve, the acetonitrile/water ratio may be increased or decreased to obtain the correct elution time. If the elution time is too long, increase the ratio; if it is too short, decrease the ratio. [Note: The chromatographic conditions described here have been optimized for the detection of formaldehyde. Analysts are advised to experiment with their HPLC system to optimize chromatographic conditions for their particular analytical needs.]

11.4 HPLC Calibration

11.4.1 Calibration standards are prepared in acetonitrile from the DNPH-formaldehyde derivative. Individual stock solutions of 100 mg/L are prepared by dissolving 10 mg of solid derivative in 100 mL of mobile phase. These individual solutions are used to prepare calibration standards at concentrations spanning the range of interest.

11.4.2 Each calibration standard (at least five levels) is analyzed three times and area response is tabulated against mass injected (Figure 7). All calibration runs are performed as described for sample analyses in Section 11.3. Using the UV detector, a linear response range of approximately 0.05-20 ug/L should be achieved for 25-uL injection volumes. The results may be used to prepare a calibration curve, as illustrated in Figure 8. Linear response is indicated where a correlation coefficient of at least 0.999 for a linear least-squares fit of the data (concentration versus area response) is obtained. The retention times for each analyte should agree within 2%.

11.4.3 Once linear response has been documented, an intermediate concentration standard near the anticipated levels of each component, but at least 10 times the detection limit, should be chosen for daily calibration. The day to day response for the various components should be within 10% for analyte concentrations 1 ug/mL or greater and within 15-20% for analyte concentrations near 0.5 ug/mL. If greater variability is observed, recalibration may be required or a new calibration curve must be developed from fresh standards.

11.4.4 The response for each component in the daily calibration standard is used to calculate a response factor according to the following equation:

$$RF_c = \frac{C_c \times V_I}{R_c}$$

where:

RF_c = response factor (usually area counts) for the component of interest in nanograms injected/response unit.

C_c = concentration (mg/L) of analyte in the daily calibration standard.

V_I = volume (uL) of calibration standard injected.

R_c = response (area counts) for analyte in the calibration standard.

12. Calculations

12.1 The total mass of analyte (DNPH-formaldehyde) is calculated for each sample using the following equation:

$$W_d = RF_c \times R_d \times V_E/V_I$$

where:

W_d = total quantity of analyte (ug) in the sample.

RF_c = response factor calculated in Section 11.4.4.

R_d = response (area counts or other response units) for analyte in sample extract, blank corrected.

= $[(A_s)(V_D/V_A) - (A_b)(V_b/V_s)]$

where:

A_s = area counts, sample.

A_b = area counts, blank.

V_b = volume (mL), blank.

V_s = volume (mL), sample.

V_E = final volume (mL) of sample extract.

V_I = volume of extract (uL) injected into the HPLC system.

V_D = redilution volume (if sample was rediluted).

V_A = aliquot used for redilution (if sample was rediluted).

12.2 The concentration of formaldehyde in the original sample is calculated from the following equation:

$$C_A = \frac{W_d}{V_m \text{ (or } V_s)} \times 1000$$

where:

C_A = concentration of analyte (ng/L) in the original sample.

W_d = total quantity of analyte (ug) in sample, blank corrected.

V_m = total sample volume (L) under ambient conditions

V_s = total sample volume (L) at 25°C and 760 mm Hg.

The analyte concentrations can be converted to ppbv using the following equation:

$$C_A \text{ (ppbv)} = C_A \text{ (ng/L)} \times \frac{24.4}{MW_A}$$

where:

C_A(ppbv) = Concentration of analyte in parts per billion by volume.

C_A (ng/L) is calculated using V_s.

MW_A = molecular weight of analyte.

13. Performance Criteria and Quality Assurance

This section summarizes required quality assurance measures and provides guidance concerning performance criteria that should be achieved within each laboratory.

13.1 Standard Operating Procedures (SOPs).

13.1.1 Users should generate SOPs describing the following activities in their laboratory: (1) assembly, calibration, and operation of the sampling system, with make and model of equipment used; (2) preparation, purification, storage, and handling of sampling reagent and samples; (3) assembly, calibration, and operation of the HPLC system, with make and model of equipment used; and (4) all aspects of data recording and processing, including lists of computer hardware and software used.

13.1.2 SOPs should provide specific stepwise instructions and should be readily available to and understood by the laboratory personnel conducting the work.

13.2 HPLC System Performance

13.2.1 The general appearance of the HPLC system should be similar to that illustrated in Figure 1.

13.2.2 HPLC system efficiency is calculated according to the following equation:

$$N = 5.54 \left(\frac{t_r}{W_{1/2}} \right)^2$$

where:

N = column efficiency (theoretical plates).

t_r = retention time (seconds) of analyte.

$W_{1/2}$ = width of component peak at half height (seconds).

A column efficiency of >5,000 theoretical plates should be obtained.

13.2.3 Precision of response for replicate HPLC injections should be $\pm$10% or less, day to day, for analyte calibration standards at 1 ug/mL or greater levels. At 0.5 ug/mL level and below, precision of replicate analyses could vary up to 25%. Precision of retention times should be $\pm$2% on a given day.

13.3 Process Blanks

13.3.1 At least one field blank or 10% of the field samples, whichever is larger, should be shipped and analyzed with each group of samples. The number of samples within a group and/or time frame should be recorded so that a specified percentage of blanks is obtained for a given number of field samples. The field blank is treated identically to the samples except that no air is drawn through the cartridge. The performance criteria described in Section 9.1 should be met for process blanks.

13.4 Method Precision and Accuracy

13.4.1 At least one duplicate sample or 10% of the field samples, whichever is larger, should be collected during each sampling episode. Precision for field replication should be ±20% or better.

13.4.2 Precision for replicate HPLC injections should be ±10% or better, day to day, for calibration standards.

13.4.3 At least one sample spike with analyte of interest or 10% of the field samples, whichever is larger, should be collected.

13.4.4 Before initial use of the method, each laboratory should generate triplicate spiked samples at a minimum of three concentration levels, bracketing the range of interest for each compound. Triplicate nonspiked samples must also be processed. Spike recoveries of >80 ± 10% and blank levels as outlined in Section 9.1 should be achieved.

14. Detection of other Aldehydes and Ketones

[Note: The procedure outlined above has been written specifically for the sampling and analysis of formaldehyde in ambient air using an adsorbent cartridge and HPLC. Ambient air contains other aldehydes and ketones. Optimizing chromatographic conditions by using two Zorbax ODS columns in series and varying the mobile phase composition through a gradient program will enable the analysis of other aldehydes and ketones.]

14.1 Sampling Procedures

Same as Section 10.

14.2 HPLC Analysis

14.2.1 The HPLC system is assembled and calibrated as described in Section 11. The operating parameters are as follows:

Column:	Zorbax ODS, two columns in series
Mobile Phase:	Acetonitrile/water, linear gradient
Step 1.	60-75% acetonitrile/40-25% water in 30 minutes.
Step 2.	75-100% acetonitrile/25-0% water in 20 minutes.
Step 3.	100% acetonitrile for 5 minutes.
Step 4.	60% acetonitrile/40% water reverse gradient in 1 minute.
Step 5.	60% acetonitrile/40% water, isocratic, for 15 minutes.
Detector:	Ultraviolet, operating at 360 nm
Flow Rate:	1.0 mL/min
Sample Injection Volume:	25 uL

14.2.2 The gradient program allows for optimization of chromatographic conditions to separate acrolein, acetone, propionaldehyde, and other higher molecular weight aldehydes and ketones in an analysis time of about one hour. Table 1 illustrates the sensitivity for selective aldehydes and ketones that have been identified using two Zorbax ODS columns in series.

14.2.3 The chromatographic conditions described here have been optimized for a gradient HPLC (Varian Model 5000) system equipped with a UV detector (ISCO Model 1840 variable wavelength), an automatic sampler with a 25-uL loop injector and two DuPont Zorbax ODS columns (4.6 x 250 mm), a recorder, and an electronic integrator. Analysts are advised to experiment with their HPLC systems to optimize chromatographic conditions for their particular analytical needs. Highest chromatographic resolution and sensitivity are desirable but may not be achieved.

The separation of acrolein, acetone, and propionaldehyde should be a minimum goal of the optimization.

14.2.4 The carbonyl compounds in the sample are identified and quantified by comparing their retention times and area counts with those of standard DNPH derivatives. Formaldehyde, acetaldehyde, acetone, propionaldehyde, crotonaldehyde, benzaldehyde, and o-, m-, p-tolualdehydes can be identified with a high degree of confidence. The identification of butyraldehyde is less certain because it coelutes with isobutyraldehyde and methyl ethyl ketone under the stated chromatographic conditions. Figure 10 illustrates a typical chromatogram obtained with the gradient HPLC system.

14.2.5 The concentrations of individual carbonyl compounds are determined as outlined in Section 12.

14.2.6 Performance criteria and quality assurance activities should meet those requirements outlined in Section 13.

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13. A.P. Altshuller and I.R. Cohen, Science 7, 1043 (1963).

14. Committee on Aldehydes, Board of Toxicology and Environmental Hazards, National Research Council, "Formaldehyde and Other Aldehydes" (National Academy Press, Washington, DC, 1981).

TABLE 1. SENSITIVITY (PPB,V/V) OF SAMPLING/ANALYSIS FOR ALDEHYDES AND KETONES IN AMBIENT AIR USING ADSORBENT CARTRIDGE FOLLOWED BY GRADIENT HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

Sample Volume, L	10	20	30	40	50	60	100	200	300	400	500	1000
Compound	Sensitivity (ppb, v/v) of DNPH/HPLC Method Carbonyls in Ambient Air											
Formaldehyde	1.45	0.73	0.48	0.36	0.29	0.24	0.15	0.07	0.05	0.04	0.03	0.01
Acetaldehyde	1.36	0.68	0.45	0.34	0.27	0.23	0.14	0.07	0.05	0.03	0.03	0.01
Acrolein	1.29	0.65	0.43	0.32	0.26	0.22	0.13	0.06	0.04	0.03	0.03	0.01
Acetone	1.28	0.64	0.43	0.32	0.26	0.21	0.13	0.06	0.04	0.03	0.03	0.01
Propionaldehyde	1.28	0.64	0.43	0.32	0.26	0.21	0.13	0.06	0.04	0.03	0.03	0.01
Crotonaldehyde	1.22	0.61	0.41	0.31	0.24	0.20	0.12	0.06	0.04	0.03	0.03	0.01
Butyraldehyde	1.21	0.61	0.40	0.30	0.24	0.20	0.12	0.06	0.04	0.03	0.02	0.01
Benzaldehyde	1.07	0.53	0.36	0.27	0.21	0.18	0.11	0.05	0.04	0.03	0.02	0.01
Isovaleraldehyde	1.15	0.57	0.38	0.29	0.23	0.19	0.11	0.06	0.04	0.03	0.02	0.01
Valeraldehyde	1.15	0.57	0.38	0.29	0.23	0.19	0.11	0.06	0.04	0.03	0.02	0.01
o-tolualdehyde	1.02	0.51	0.34	0.25	0.20	0.17	0.10	0.05	0.03	0.03	0.02	0.01
m-tolualdehyde	1.02	0.51	0.34	0.25	0.20	0.17	0.10	0.05	0.03	0.03	0.02	0.01
p-tolualdehyde	1.02	0.51	0.34	0.25	0.20	0.17	0.10	0.05	0.03	0.03	0.02	0.01
Hexanaldehyde	1.09	0.55	0.36	0.27	0.22	0.18	0.11	0.05	0.04	0.03	0.02	0.01
2,5-Dimethylbenzaldehyde	0.97	0.49	0.32	0.24	0.19	0.16	0.10	0.05	0.03	0.02	0.02	0.01

[Note: Ppb values are measured at 1 atm and 25°C; sample cartridge is eluted with 5 mL acetonitrile, and 25 mL are injected onto HPLC column.]

[Note: Maximum sampling flow through a DNPH-coated SEP-PAK is about 1.5 L per minute.]

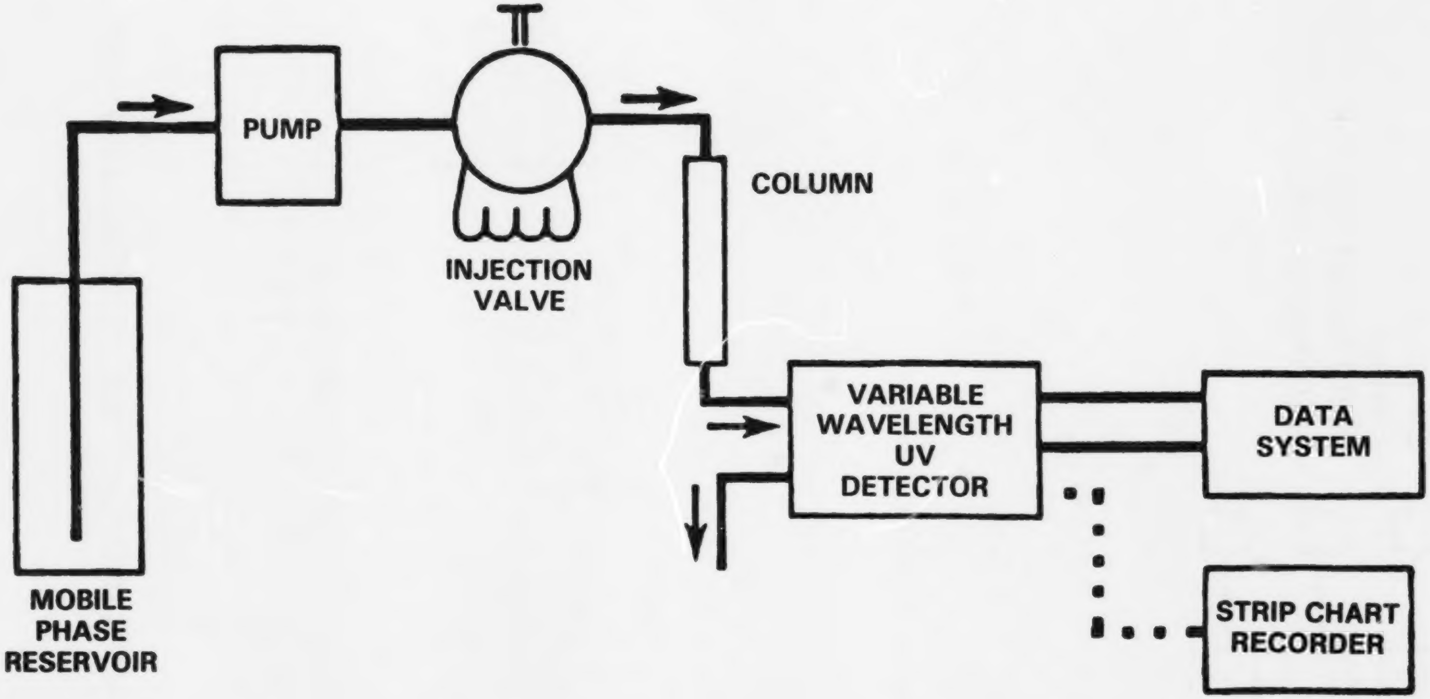
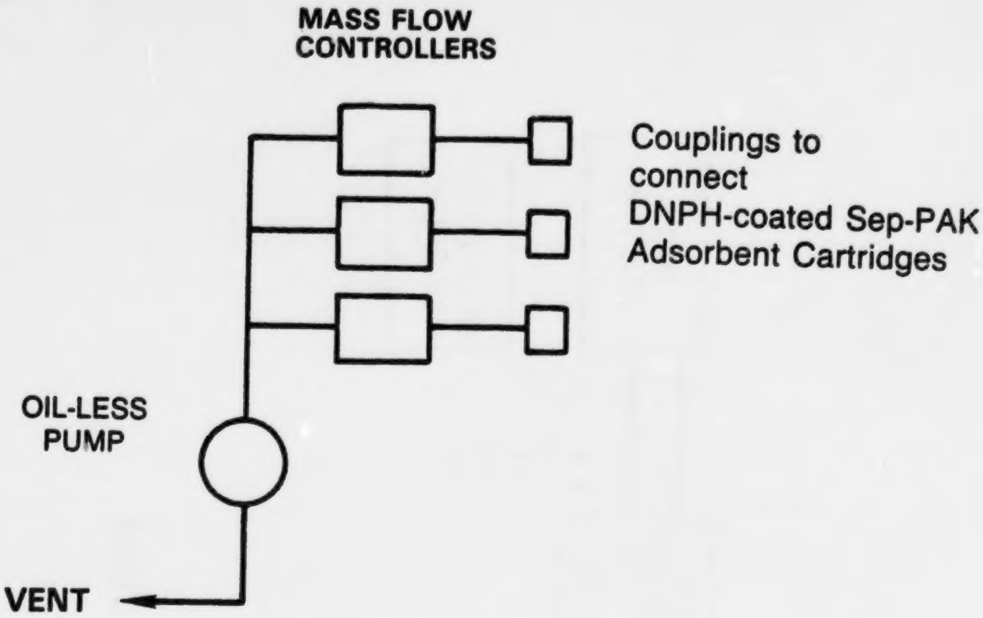
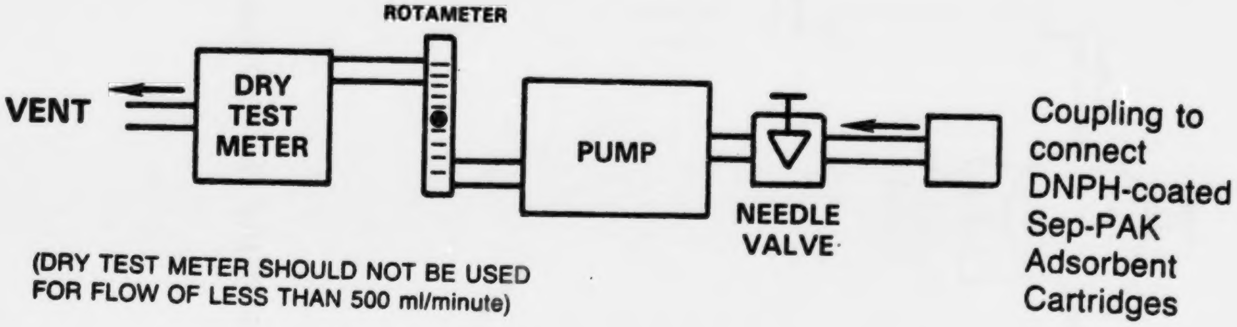

PUMP
COLUMN
INJECTION VALVE
VARIABLE WAVELENGTH UV DETECTOR
DATA SYSTEM
MOBILE PHASE RESERVOIR
STRIP CHART RECORDER

FIGURE 1. TYPICAL HPLC SYSTEM


MASS FLOW
CONTROLLERS
Couplings to
connect
DNPH-coated Sep-PAK
Adsorbent Cartridges
OIL-LESS
PUMP
VENT

(a) MASS FLOW CONTROL


ROTAMETER
VENT
DRY
TEST
METER
PUMP
NEEDLE
VALVE
Coupling to
connect
DNPH-coated
Sep-PAK
Adsorbent
Cartridges
(DRY TEST METER SHOULD NOT BE USED
FOR FLOW OF LESS THAN 500 ml/minute)

(b) NEEDLE VALVE/DRY TEST METER

FIGURE 2. TYPICAL SAMPLING SYSTEM CONFIGURATIONS

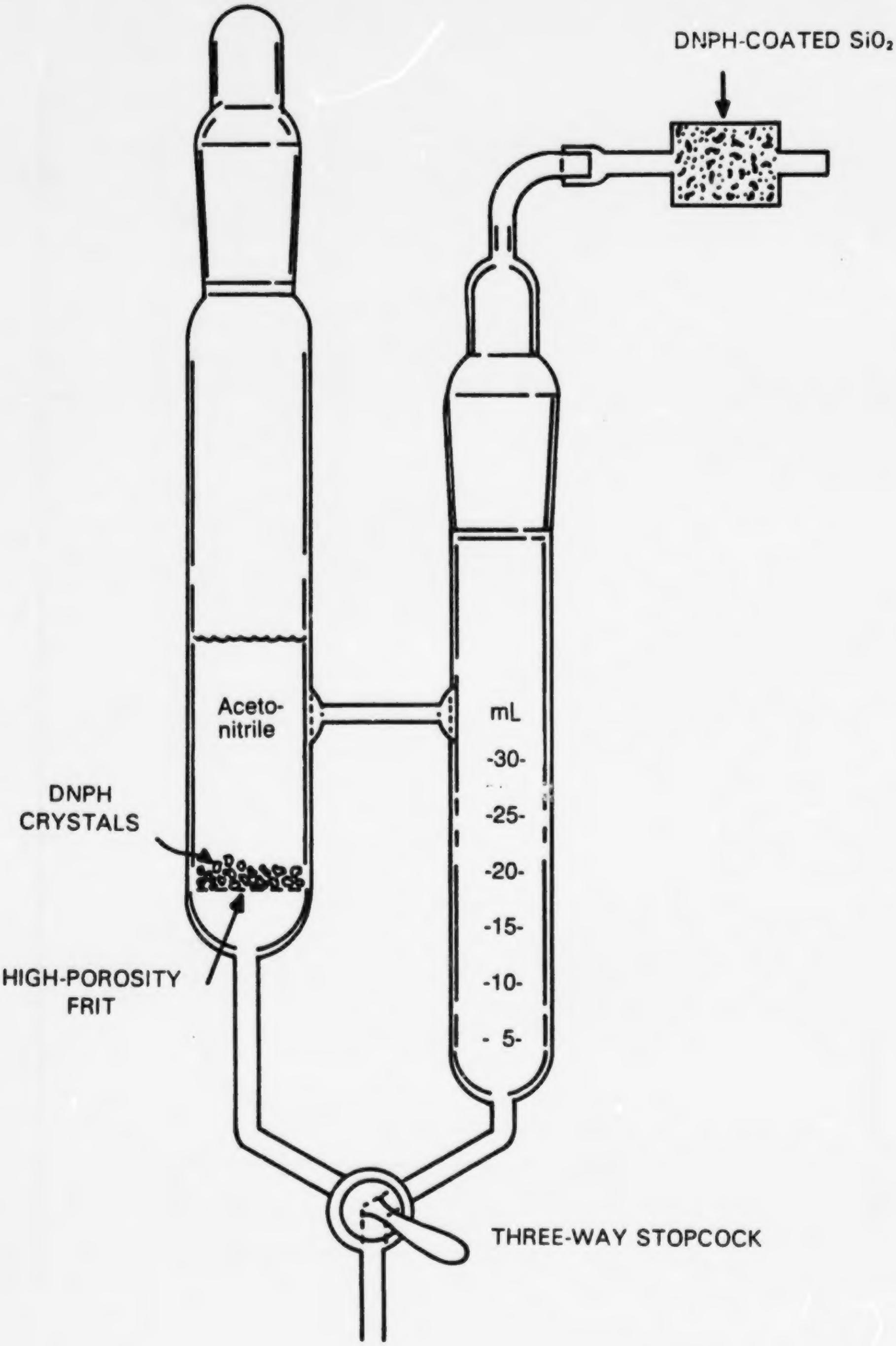

DNPH-COATED SiO₂
Aceto-nitrile
DNPH CRYSTALS
HIGH-POROSITY FRIT
mL
-30-
-25-
-20-
-15-
-10-
- 5-
THREE-WAY STOPCOCK

FIGURE 3. **SPECIAL GLASS APPARATUS FOR RINSING, STORING, AND DISPENSING SATURATED DNPH STOCK SOLUTION**

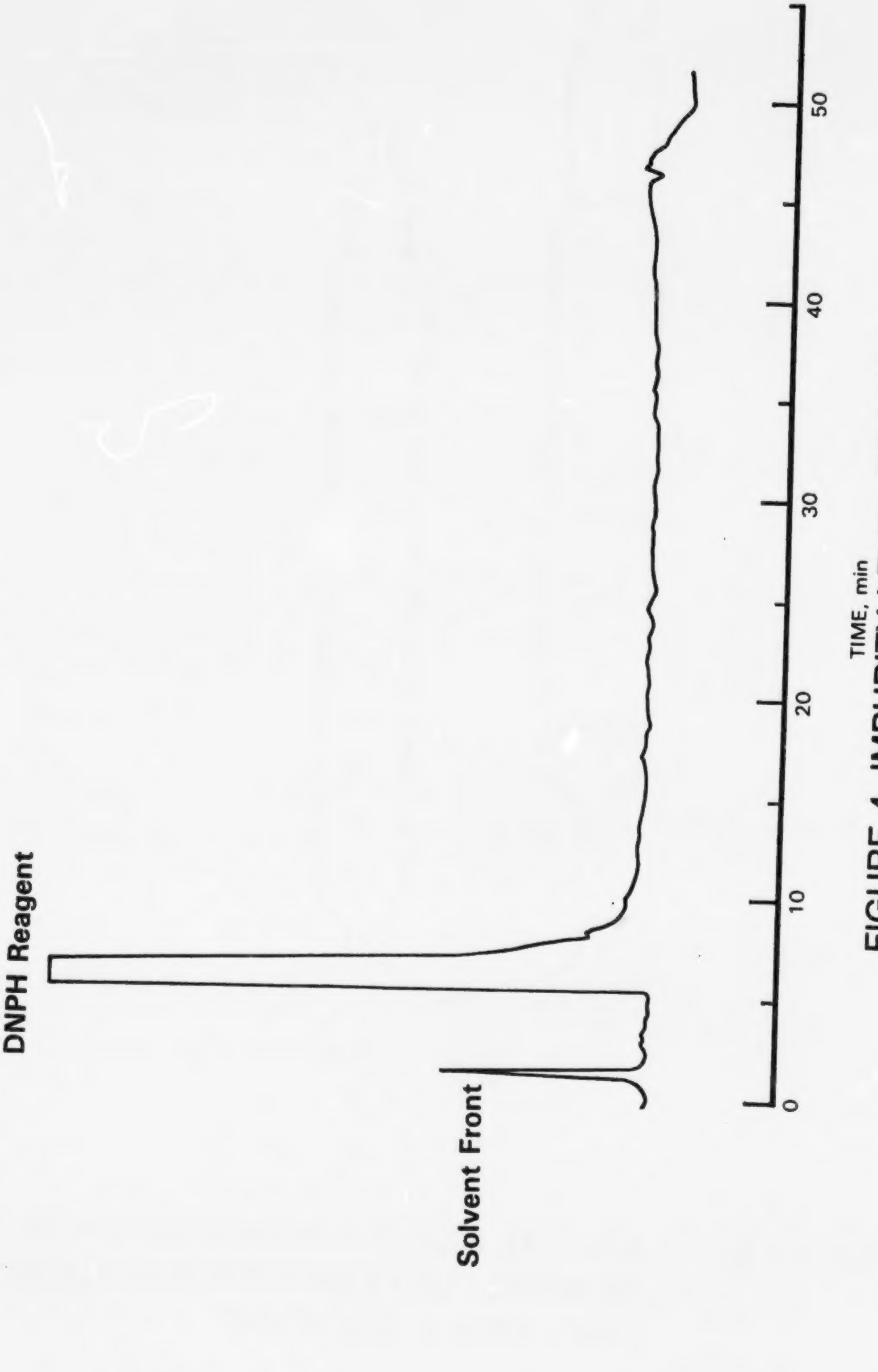


FIGURE 4. IMPURITY LEVEL OF DNPH AFTER RECRYSTALLIZATION

SAMPLING DATA SHEET
(One Sample per Data Sheet)

PROJECT: ____________________ DATE(S) SAMPLED: ____________________

SITE: ____________________ TIME PERIOD SAMPLED: ____________________

LOCATION: ____________________ OPERATOR: ____________________

INSTRUMENT MODEL NO: ____________________ CALIBRATED BY: ____________________

PUMP SERIAL NO: ____________________

ADSORBENT CARTRIDGE INFORMATION:

Type: ____________________ Serial Number: ____________________

Adsorbent: ____________________ Sample Number: ____________________

SAMPLING DATA:

Start Time: ____________________ Stop Time: ____________________

Time	Dry Gas Meter Reading	Rotameter Reading	Flow Rate (Q)*, mL/min	Ambient Temperature, °C	Barometric Pressure, mm Hg	Relative Humidity,%	Comments
Avg.							

* Flow rate from rotameter or soap bubble calibrator (specify which)

Total Volume Data (V_m) (use data from dry gas meter, if available)

V_m = (Final - Initial) Dry Gas Meter Reading, or = ______ Liters

or

$$V_m = \frac{Q_1 + Q_2 + Q_3 \ldots Q_N}{N} \times \frac{1}{1000 \times (\text{Sampling Time in Minutes})} = \underline{\qquad} \text{ Liters}$$

FIGURE 5. EXAMPLE SAMPLING DATA SHEET

OPERATING PARAMETERS
HPLC

Column: Zorbax ODS or C-18 RP
Mobile Phase: 60% Acetonitrile/40% Water
Detector: Ultraviolet, operating at 360 nm
Flow Rate: 1 mL/min.
Retention Time: ~ 7 minutes for formaldehyde
Sample Injection Volume: 25 uL

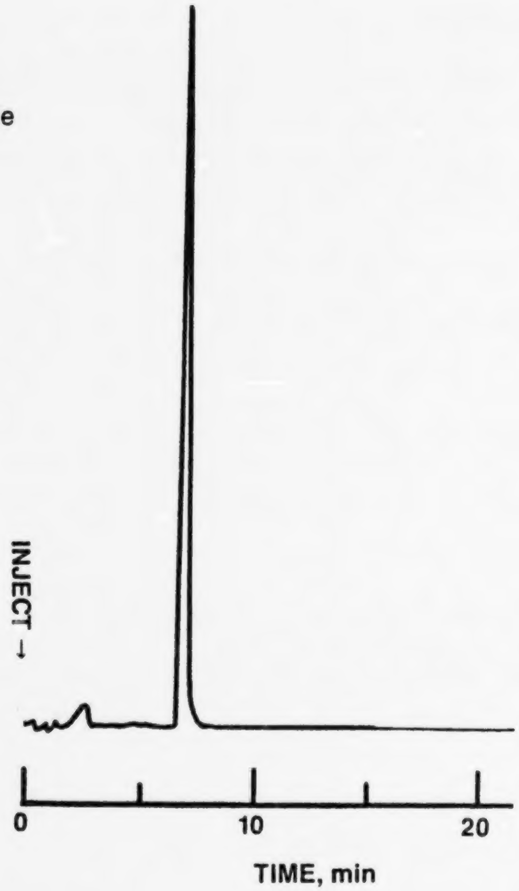
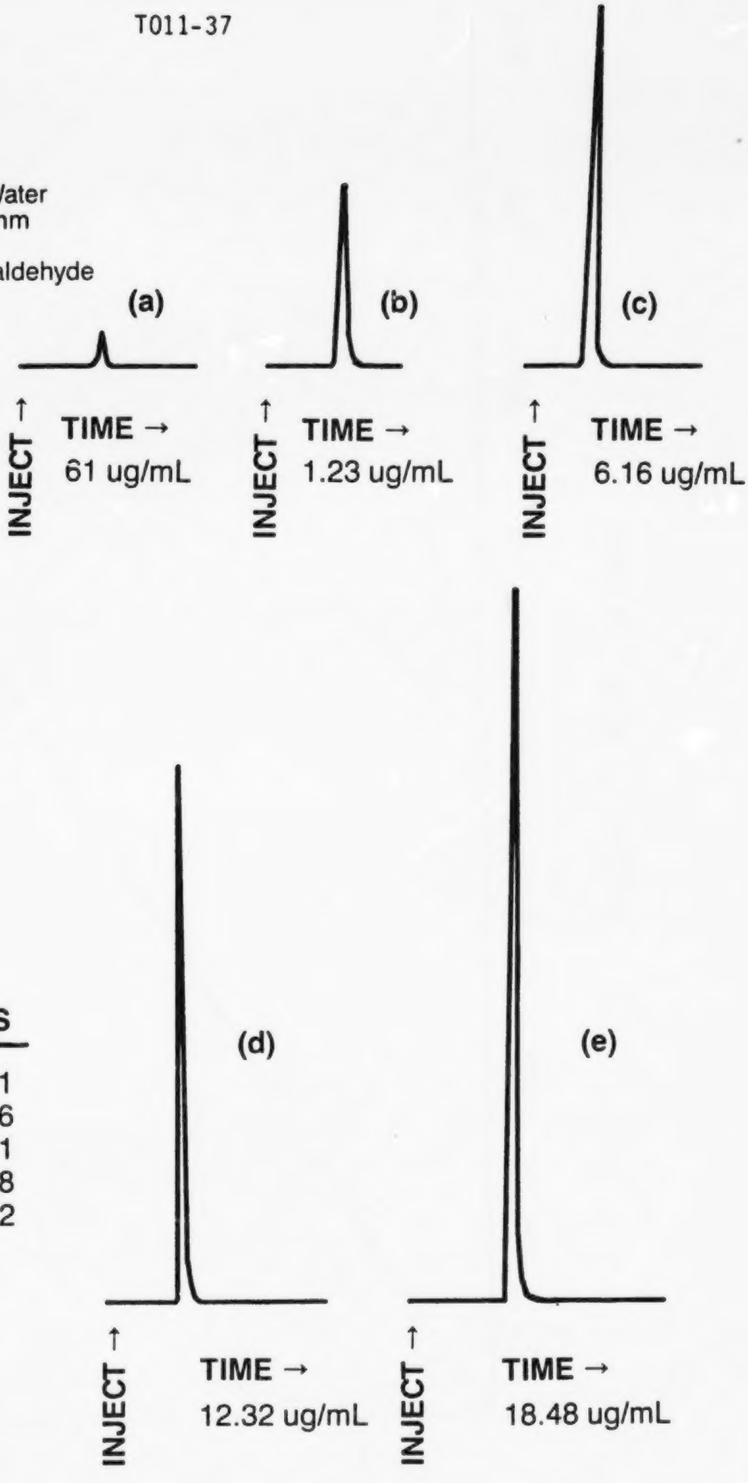


FIGURE 6. CHROMATOGRAM OF DNPH-FORMALDEHYDE DERIVATIVE

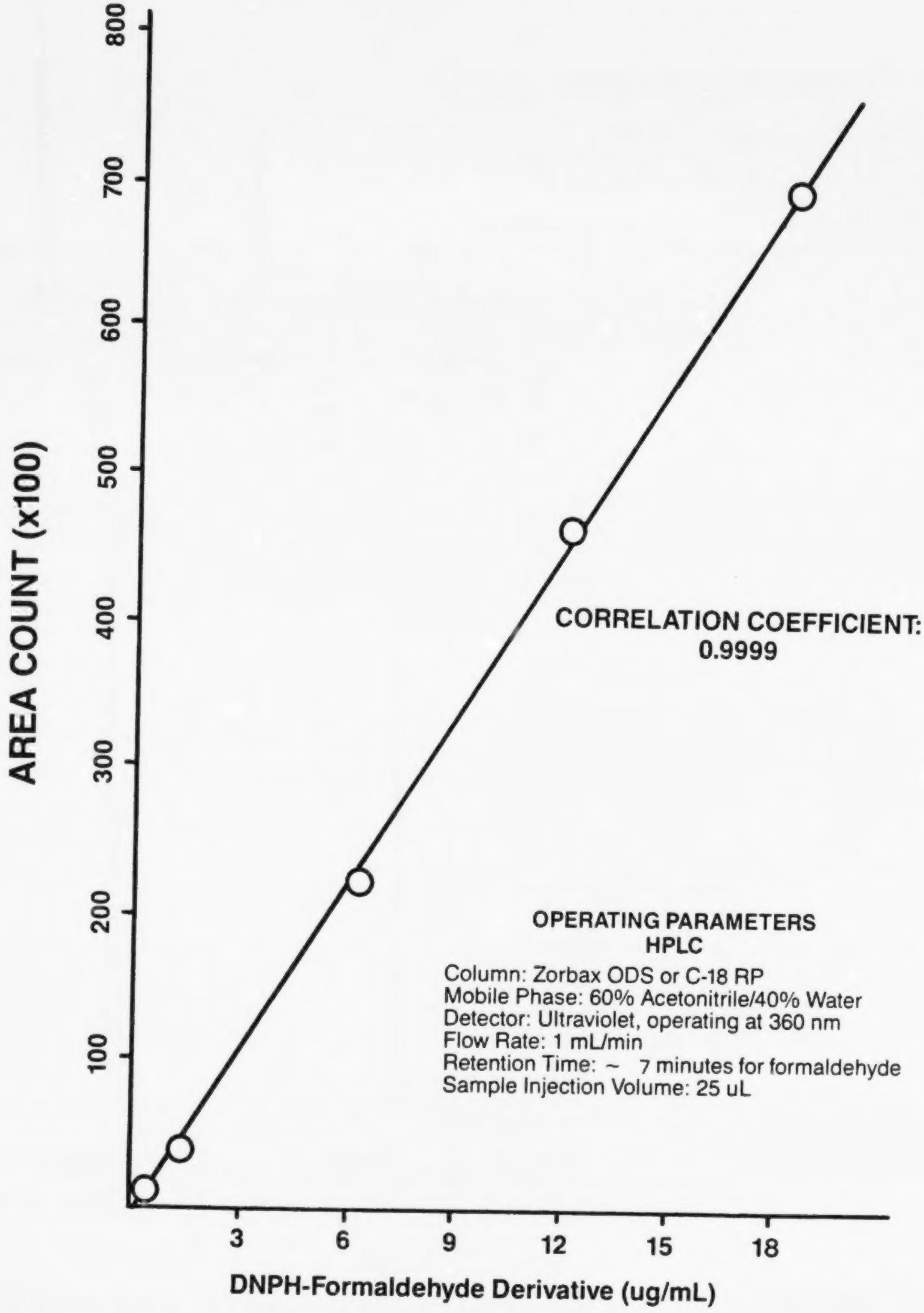
OPERATING PARAMETERS
HPLC

Column: Zorbax ODS or C-18 RP
Mobile Phase: 60% Acetonitrile/40% Water
Detector: Ulltraviolet, operating at 360 nm
Flow Rate: 1 mL/min.
Retention Time: ~ 7 minutes for formaldehyde
Sample Injection Volume: 25 uL



CONC	AREA COUNTS
.61 ug/mL	226541
1.23 ug/mL	452166
6.16 ug/mL	2257271
12.32 ug/mL	4711408
18.48 ug/mL	6953812

FIGURE 7. HPLC CHROMATOGRAM OF VARYING CONCENTRATIONS OF DNPH-FORMALDEHYDE DERIVATIVE



CORRELATION COEFFICIENT:
0.9999

OPERATING PARAMETERS
HPLC

Column: Zorbax ODS or C-18 RP
Mobile Phase: 60% Acetonitrile/40% Water
Detector: Ultraviolet, operating at 360 nm
Flow Rate: 1 mL/min
Retention Time: ~ 7 minutes for formaldehyde
Sample Injection Volume: 25 uL

FIGURE 8. CALIBRATION CURVE FOR FORMALDEHYDE

METHOD T012

METHOD FOR THE DETERMINATION OF NON-METHANE ORGANIC COMPOUNDS (NMOC) IN AMBIENT AIR USING CRYOGENIC PRECONCENTRATION AND DIRECT FLAME IONIZATION DETECTION (PDFID)

1. Scope

1.1 In recent years, the relationship between ambient concentrations of precursor organic compounds and subsequent downwind concentrations of ozone has been described by a variety of photochemical dispersion models. The most important application of such models is to determine the degree of control of precursor organic compounds that is necessary in an urban area to achieve compliance with applicable ambient air quality standards for ozone (1,2).

1.2 The more elaborate theoretical models generally require detailed organic species data obtained by multicomponent gas chromatography (3). The Empirical Kinetic Modeling Approach (EKMA), however, requires only the total non-methane organic compound (NMOC) concentration data; specifically, the average total NMOC concentration from 6 a.m. to 9 a.m. daily at the sampling location. The use of total NMOC concentration data in the EKMA substantially reduces the cost and complexity of the sampling and analysis system by not requiring qualitative and quantitative species identification.

1.3 Method T01, "Method for The Determination of Volatile Organic Compounds in Ambient Air Using Tenax® Adsorption and Gas Chromatography/Mass Spectrometry (GC/MS)", employs collection of certain volatile organic compounds on Tenax® GC with subsequent analysis by thermal desorption/cryogenic preconcentration and GC/MS identification. This method (T012) combines the same type of cryogenic concentration technique used in Method T01 for high sensitivity with the simple flame ionization detector (FID) of the GC for total NMOC measurements, without the GC columns and complex procedures necessary for species separation.

1.4 In a flame ionization detector, the sample is injected into a hydrogen-rich flame where the organic vapors burn producing ionized molecular fragments. The resulting ion fragments are then collected and detected. The FID is nearly a universal detector. However, the detector response varies with the species of [functional group in] the organic compound in an oxygen atmosphere. Because this method employs a helium or argon carrier gas, the detector response is nearly one for all compounds. Thus, the historical short-coming of the FID involving varying detector response to different organic functional groups is minimized.

1.5 The method can be used either for direct, in situ ambient measurements or (more commonly) for analysis of integrated samples collected in specially treated stainless steel canisters. EKMA models generally require 3-hour integrated NMOC measurements over the 6 a.m. to 9 a.m. period and are used by State or local agencies to prepare State Implementation Plans (SIPs) for ozone control to achieve compliance with the National Ambient Air Quality Standards (NAAQS) for ozone. For direct, in situ ambient measurements, the analyst must be present during the 6 a.m. to 9 a.m. period, and repeat measurements (approximately six per hour) must be taken to obtain the 6 a.m. to 9 a.m. average NMOC concentration. The use of sample canisters allows the collection of integrated air samples over the 6 a.m. to 9 a.m. period by unattended, automated samplers. This method has incorporated both sampling approaches.

2. Applicable Documents

2.1 ASTM Standards

D1356 - Definition of Terms Related to Atmospheric Sampling and Analysis

E260 - Recommended Practice for General Gas Chromatography Procedures

E355 - Practice for Gas Chromatography Terms and Relationships

2.2 Other Documents

U. S. Environmental Protection Agency Technical Assistance Documents (4,5)
Laboratory and Ambient Air Studies (6-10)

3. Summary of Method

3.1 A whole air sample is either extracted directly from the ambient air and analyzed on site by the GC system or collected into a precleaned sample canister and analyzed off site.

3.2 The analysis requires drawing a fixed-volume portion of the sample air at a low flow rate through a glass-bead filled trap that is cooled to approximately -186°C with liquid argon. The cryogenic trap simultaneously collects and concentrates the NMOC (either via condensation or adsorption) while allowing the methane, nitrogen, oxygen, etc. to pass through the trap without retention. The system is dynamically calibrated so that the volume of sample passing through the trap does not have to be quantitatively measured, but must be precisely repeatable between the calibration and the analytical phases.

3.3 After the fixed-volume air sample has been drawn through the trap, a helium carrier gas flow is diverted to pass through the trap, in the opposite direction to the sample flow, and into an FID. When the residual air and methane have been flushed from the trap and the FID baseline restabilizes, the cryogen is removed and the temperature of the trap is raised to approximately 90°C.

3.4 The organic compounds previously collected in the trap revolatilize due to the increase in temperature and are carried into the FID, resulting in a response peak or peaks from the FID. The area of the peak or peaks is integrated, and the integrated value is translated to concentration units via a previously-obtained calibration curve relating integrated peak areas with known concentrations of propane.

3.5 By convention, concentrations of NMOC are reported in units of parts per million carbon (ppmC), which, for a specific compound, is the concentration by volume (ppmV) multiplied by the number of carbon atoms in the compound.

3.6 The cryogenic trap simultaneously concentrates the NMOC while separating and removing the methane from air samples. The technique is thus direct reading for NMOC and, because of the concentration step, is more sensitive than conventional continuous NMOC analyzers.

4. Significance

4.1 Accurate measurements of ambient concentrations of NMOC are important for the control of photochemical smog because these organic compounds are primary precursors of atmospheric ozone and other oxidants. Achieving and maintaining compliance with the NAAQS for ozone thus depends largely on control of ambient levels of NMOC.

4.2 The NMOC concentrations typically found at urban sites may range up to 5-7 ppmC or higher. In order to determine transport of precursors into an area, measurement of NMOC upwind of the area may be necessary. Upwind NMOC concentrations are likely to be less than a few tenths of 1 ppm.

4.3 Conventional methods that depend on gas chromatography and qualitative and quantitative species evaluation are excessively difficult and expensive to operate and maintain when speciated measurements are not needed. The method described here involves a simple, cryogenic preconcentration procedure with subsequent, direct, flame ionization detection. The method is sensitive and provides accurate measurements of ambient NMOC concentrations where speciated data are not required as applicable to the EKMA.

5. Definitions

[Note: Definitions used in this document and in any user-prepared Standard Operating Procedures (SOPs) should be consistent with ASTM Methods D1356 and E355. All abbreviations and symbols are defined within this document at point of use.]

5.1 Absolute pressure - Pressure measured with reference to absolute zero pressure (as opposed to atmospheric pressure), usually expressed as pounds-force per square inch absolute (psia).

5.2 Cryogen - A substance used to obtain very low trap temperatures in the NMOC analysis system. Typical cryogens are liquid argon (bp -185.7) and liquid oxygen (bp-183.0).

5.3 Dynamic calibration - Calibration of an analytical system with pollutant concentrations that are generated in a dynamic, flowing system, such as by quantitative, flow-rate dilution of a high concentration gas standard with zero gas.

5.4 EKMA - Empirical Kinetics Modeling Approach; an empirical model that attempts to relate morning ambient concentrations of nonmethane organic compounds (NMOC) and NO_x with subsequent peak, downwind ambient ozone concentrations; used by pollution control agencies to estimate the degree of hydrocarbon emission reduction needed to achieve compliance with national ambient air quality standards for ozone.

5.5 Gauge pressure - Pressure measured with reference to atmospheric pressure (as opposed to absolute pressure). Zero gauge pressure (0 psig) is equal to atmospheric pressure, or 14.7 psia (101 kPa).

5.6 *In situ* - In place; *In situ* measurements are obtained by direct, on-the-spot analysis, as opposed to subsequent, remote analysis of a collected sample.

5.7 Integrated sample - A sample obtained uniformly over a specified time period and representative of the average levels of pollutants during the time period.

5.8 NMOC - Nonmethane organic compounds; total organic compounds as measured by a flame ionization detector, excluding methane.

5.9 ppmC - Concentration unit of parts per million carbon; for a specific compound, ppmC is equivalent to parts per million by volume (ppmv) multiplied by the number of carbon atoms in the compound.

5.10 Sampling - The process of withdrawing or isolating a representative portion of an ambient atmosphere, with or without the simultaneous isolation of selected components for subsequent analysis.

6. Interferences

6.1 In field and laboratory evaluation, water was found to cause a positive shift in the FID baseline. The effect of this shift is minimized by carefully selecting the integration termination point and adjusted baseline used for calculating the area of the NMOC peak(s).

6.2 When using helium as a carrier gas, FID response is quite uniform for most hydrocarbon compounds, but the response can vary considerably for other types of organic compounds.

7. Apparatus

7.1 Direct Air Sampling (Figure 1)

7.1.1 Sample manifold or sample inlet line - to bring sample air into the analytical system.

7.1.2 Vacuum pump or blower - to draw sample air through a sample manifold or long inlet line to reduce inlet residence time. Maximum residence time should be no greater than 1 minute.

7.2 Remote Sample Collection in Pressurized Canisters (Figure 2)

7.2.1 Sample canister(s) - stainless steel, Summa®-polished vessel(s) of 4-6 L capacity (Scientific Instrumentation Specialists, Inc., P.O. Box 8941, Moscow, ID 83843), used for automatic collection of 3-hour integrated field air samples. Each canister should have a unique identification number stamped on its frame.

7.2.2 Sample pump - stainless steel, metal bellows type (Model MB-151, Metal Bellows Corp., 1075 Providence Highway, Sharon, MA 02067) capable of 2 atmospheres minimum output pressure. Pump must be free of leaks, clean, and uncontaminated by oil or organic compounds.

7.2.3 Pressure gauge - 0-30 psig (0-240 kPa).

7.2.4 Solenoid valve - special electrically-operated, bistable solenoid valve (Skinner Magnelatch Valve, New Britain, CT), to control sample flow to the canister with negligible temperature rise (Figure 3). The use of the Skinner Magnelatch valve avoids any substantial temperature rise that would occur with a conventional, normally closed solenoid valve, which would have to be energized during the entire sample period. This temperature rise in the valve could cause outgasing of organics from the Viton valve seat material. The Skinner Magnelatch valve requires only a brief electrical pulse to open or close at the appropriate start and stop times and therefore experiences no temperature increase. The pulses may be obtained with an electronic timer that can be programmed for short (5 to 60 seconds) ON periods or with a conventional mechanical timer and a special pulse circuit. Figure 3 [a] illustrates a simple electrical pulse circuit for operating the Skinner Magnelatch solenoid valve with a conventional mechanical timer. However, with this simple circuit, the valve may operate unpredictably during brief power interruptions or if the timer is manually switched on and off too fast. A better circuit incorporating a time-delay relay to provide more reliable valve operation is shown in Figure 3[b].

7.2.5 Stainless steel orifice (or short capillary) - capable of maintaining a substantially constant flow over the sampling period (see Figure 4).

7.2.6 Particulate matter filter - 2 micron stainless steel sintered in-line type (see Figure 4).

7.2.7 Timer - used for unattended sample collection. Capable of controlling pump(s) and solenoid valve.

7.3 Sample Canister Cleaning (Figure 5)

7.3.1 Vacuum pump - capable of evacuating sample canister(s) to an absolute pressure of <5 mm Hg.

7.3.2 Manifold - stainless steel manifold with connections for simultaneously cleaning several canisters.

7.3.3 Shut off valve(s) - seven required.

7.3.4 Vacuum gauge - capable of measuring vacuum in the manifold to an absolute pressure of 5 mm Hg or less.

7.3.5 Cryogenic trap (2 required) - U-shaped open tubular trap cooled with liquid nitrogen or argon used to prevent contamination from back diffusion of oil from vacuum pump, and to provide clean, zero air to sample canister(s).

7.3.6 Pressure gauge - 0-50 psig (0-345 kPa), to monitor zero air pressure.

7.3.7 Flow control valve - to regulate flow of zero air into canister(s).

7.3.8 Humidifier - water bubbler or other system capable of providing moisture to the zero air supply.

7.4 Analytical System (Figure 1)

7.4.1 FID detector system - including flow controls for the FID fuel and air, temperature control for the FID, and signal processing electronics. The FID burner air, hydrogen, and helium carrier flow rates should be set according to the manufacturer's instructions to obtain an adequate FID response while maintaining as stable a flame as possible throughout all phases of the analytical cycle.

7.4.2 Chart recorder - compatible with the FID output signal, to record FID response.

7.4.3 Electronic integrator - capable of integrating the area of one or more FID response peaks and calculating peak area corrected for baseline drift. If a separate integrator and chart recorder are used, care must be exercised to be sure that these components do not interfere with each other electrically. Range selector controls on both the integrator and the FID analyzer may not provide accurate range ratios, so individual calibration curves should be prepared for each range to be used. The integrator should be capable of marking the beginning and ending of peaks, constructing the appropriate baseline between the start and end of the integration period, and calculating the peak area.

Note: The FID (7.4.1), chart recorder (7.4.2), integrator (7.4.3), valve heater (7.4.5), and a trap heating system are conveniently provided by a standard laboratory chromatograph and associated integrator. EPA has adapted two such systems for the PDFID method: a Hewlett-Packard model 5880 (Hewlett-Packard Corp., Avondale, PA) and a Shimadzu model GC8APF (Shimadzu Scientific Instruments Inc., Columbia, MD; see Reference 5). Other similar systems may also be applicable.

7.4.4 Trap - the trap should be carefully constructed from a single piece of chromatographic-grade stainless steel tubing (0.32 cm O.D, 0.21 cm I.D.) as shown in Figure 6. The central portion of the trap (7-10 cm) is packed with 60/80 mesh glass beads, with small glass wool (dimethyldichlorosilane-treated) plugs to retain the beads. The trap must fit conveniently into the Dewar flask (7.4.9), and the arms must be of an appropriate length to allow the beaded portion of the trap to be submerged below the level of liquid cryogen in the Dewar. The trap should connect directly to the six-port valve, if possible, to minimize line length between the trap and the FID. The trap must be mounted to allow the Dewar to be slipped conveniently on and off the trap and also to facilitate heating of the trap (see 7.4.13).

7.4.5 Six-port chromatographic valve - Seiscor Model VIII (Seismograph Service Corp., Tulsa, OK), Valco Model 9110 (Valco Instruments Co., Houston, TX), or equivalent. The six-port valve and as much of the interconnecting tubing as practical should be located inside an oven or otherwise heated to 80 - 90°C to minimize wall losses or adsorption/desorption in the connecting tubing. All lines should be as short as practical.

7.4.6 Multistage pressure regulators - standard two-stage, stainless steel diaphram regulators with pressure gauges, for helium, air, and hydrogen cylinders.

7.4.7 Pressure regulators - optional single stage, stainless steel, with pressure gauge, if needed, to maintain constant helium carrier and hydrogen flow rates.

7.4.8 Fine needle valve - to adjust sample flow rate through trap.

7.4.9 Dewar flask - to hold liquid cryogen to cool the trap, sized to contain submerged portion of trap.

7.4.10 Absolute pressure gauge - 0-450 mm Hg,(2 mm Hg [scale divisions indicating units]), to monitor repeatable volumes of sample air through cryogenic trap (Wallace and Tiernan, Model 61C-ID-0410, 25 Main Street, Belleville, NJ).

7.4.11 Vacuum reservoir - 1-2 L capacity, typically 1 L.

7.4.12 Gas purifiers - gas scrubbers containing Drierite® or silica gel and 5A molecular sieve to remove moisture and organic impurities in the helium, air, and hydrogen gas flows (Alltech Associates, Deerfield, IL). Note: Check purity of gas purifiers prior to use by passing zero-air through the unit and analyzing according to Section 11.4. Gas purifiers are clean if produce [contain] less than 0.02 ppmC hydrocarbons.

7.4.13 Trap heating system - chromatographic oven, hot water, or other means to heat the trap to 80° to 90°C. A simple heating source for the trap is a beaker or Dewar filled with water maintained at 80-90°C. More repeatable types of heat sources are recommended, including a temperature-programmed chromatograph oven, electrical heating of the trap itself, or any type of heater that brings the temperature of the trap up to 80-90°C in 1-2 minutes.

7.4.14 Toggle shut-off valves (2) - leak free, for vacuum valve and sample valve.

7.4.15 Vacuum pump - general purpose laboratory pump capable of evacuating the vacuum reservoir to an appropriate vacuum that allows the desired sample volume to be drawn through the trap.

7.4.16 Vent - to keep the trap at atmospheric pressure during trapping when using pressurized canisters.

7.4.17 Rotameter - to verify vent flow.

7.4.18 Fine needle valve (optional) - to adjust flow rate of sample from canister during analysis.

7.4.19 Chromatographic-grade stainless steel tubing (Alltech Applied Science, 2051 Waukegan Road, Deerfield, IL, 60015, (312) 948-8600) and stainless steel plumbing fittings - for interconnections. All such materials in contact with the sample, analyte, or support gases prior to analysis should be stainless steel or other inert metal. Do not use plastic or Teflon® tubing or fittings.

7.5 Commercially Available PDFID System (5)

7.5.1 A convenient and cost-effective modular PDFID system suitable for use with a conventional laboratory chromatograph is commercially available (NuTech Corporation, Model 8548, 2806 Cheek Road, Durham, NC, 27704, (919) 682-0402).

7.5.2 This modular system contains almost all of the apparatus items needed to convert the chromatograph into a PDFID analytical system and has been designed to be readily available and easy to assemble.

8. Reagents and Materials

8.1 Gas cylinders of helium and hydrogen - ultrahigh purity grade.

8.2 Combustion air - cylinder containing less than 0.02 ppm hydrocarbons, or equivalent air source.

8.3 Propane calibration standard - cylinder containing 1-100 ppm (3-300 ppmC) propane in air. The cylinder assay should be traceable to a National Bureau of Standards (NBS) Standard Reference Material (SRM) or to a NBS/EPA-approved Certified Reference Material (CRM).

8.4 Zero air - cylinder containing less than 0.02 ppmC hydrocarbons. Zero air may be obtained from a cylinder of zero-grade compressed air scrubbed with Drierite® or silica gel and 5A molecular sieve or activated charcoal, or by catalytic cleanup of ambient air. All zero air should be passed through a liquid argon cold trap for final cleanup, then passed through a hyrdocarbon-free water bubbler (or other device) for humidification.

8.5 Liquid cryogen - liquid argon (bp -185.7°C) or liquid oxygen, (bp -183°C) may be used as the cryogen. Experiments have shown no differences in trapping efficiency between liquid argon and liquid oxygen. However, appropriate safety precautions must be taken if liquid oxygen is used. Liquid nitrogen (bp -195°C) should not be used because it causes condensation of oxygen and methane in the trap.

9. Direct Sampling

9.1 For direct ambient air sampling, the cryogenic trapping system draws the air sample directly from a pump-ventilated distribution manifold or sample line (see Figure 1). The connecting line should be of small diameter (1/8" O.D.) stainless steel tubing and as short as possible to minimize its dead volume.

9.2 Multiple analyses over the sampling period must be made to establish hourly or 3-hour NMOC concentration averages.

10. Sample Collection in Pressurized Canister(s)

For integrated pressurized canister sampling, ambient air is sampled by a metal bellows pump through a critical orifice (to maintain constant flow), and pressurized into a clean, evacuated, Summa®-polished sample canister. The critical orifice size is chosen so that the canister is pressurized to approximately one atmosphere above ambient pressure, at a constant flow rate over the desired sample period. Two canisters are connected in parallel for duplicate samples. The canister(s) are then returned to the laboratory for analysis, using the PDFID analytical system. Collection of ambient air samples in pressurized canisters provides the following advantages:

- Convenient integration of ambient samples over a specific time period
- Capability of remote sampling with subsequent central laboratory analysis
- Ability to ship and store samples, if necessary

- Unattended sample collection
- Analysis of samples from multiple sites with one analytical system
- Collection of replicate samples for assessment of measurement precision

With canister sampling, however, great care must be exercised in selecting, cleaning, and handling the sample canister(s) and sampling apparatus to avoid losses or contamination of the samples.

10.1 Canister Cleanup and Preparation

10.1.1 All canisters must be clean and free of any contaminants before sample collection.

10.1.2 Leak test all canisters by pressurizing them to approximately 30 psig [200 kPa (gauge)] with zero air. The use of the canister cleaning system (see Figure 5) may be adequate for this task. Measure the final pressure - close the canister valve, then check the pressure after 24 hours. If leak tight, the pressure should not vary more than ± 2 psig over the 24-hour period. Note leak check result on sampling data sheet, Figure 7.

10.1.3 Assemble a canister cleaning system, as illustrated in Figure 5. Add cryogen to both the vacuum pump and zero air supply traps. Connect the canister(s) to the manifold. Open the vent shut off valve and the canister valve(s) to release any remaining pressure in the canister. Now close the vent shut off valve and open the vacuum shut off valve. Start the vacuum pump and evacuate the canister(s) to ≤ 5.0 mm Hg (for at least one hour). [Note: On a daily basis or more often if necessary, blow-out the cryogenic traps with zero air to remove any trapped water from previous canister cleaning cycles.]

10.1.4 Close the vacuum and vacuum gauge shut off valves and open the zero air shut off valve to pressurize the canister(s) with moist zero air to approximately 30 psig [200 kPa (gauge)]. If a zero gas generator system is used, the flow rate may need to be limited to maintain the zero air quality.

10.1.5 Close the zero shut off valve and allow canister(s) to vent down to atmospheric pressure through the vent shut off valve. Close the vent shut off valve. Repeat steps 10.1.3 through 10.1.5 two additional times for a total of three (3) evacuation/pressurization cycles for each set of canisters.

10.1.6 As a "blank" check of the canister(s) and cleanup procedure, analyze the final zero-air fill of 100% of the canisters until the cleanup system and canisters are proven reliable. The check can then be reduced to a lower percentage of canisters. Any canister that does not test clean (compared to direct analysis of humidified zero air of less than 0.02 ppmC) should not be utilized.

10.1.7 The canister is then re-evacuated to $\leq$ 5.0 mm Hg, using the canister cleaning system, and remains in this condition until use. Close the canister valve, remove the canister from the canister cleaning system and cap canister connection with a stainless steel fitting. The canister is now ready for collection of an air sample. Attach an identification tag to the neck of each canister for field notes and chain-of-custody purposes.

10.2 Collection of Integrated Whole-Air Samples

10.2.1 Assemble the sampling apparatus as shown in Figure 2. The connecting lines between the sample pump and the canister(s) should be as short as possible to minimize their volume. A second canister is used when a duplicate sample is desired for quality assurance (QA) purposes (see Section 12.2.4). The small auxiliary vacuum pump purges the inlet manifold or lines with a flow of several L/min to minimize the sample residence time. The larger metal bellows pump takes a small portion of this sample to fill and pressurize the sample canister(s). Both pumps should be shock-mounted to minimize vibration. Prior to field use, each sampling system should be leak tested. The outlet side of the metal bellows pump can be checked for leaks by attaching the 0-30 psig pressure gauge to the canister(s) inlet via connecting tubing and pressurizing to 2 atmospheres or approximately 29.4 psig. If pump and connecting lines are leak free pressure should remain at ±2 psig for 15 minutes. To check the inlet side, plug the sample inlet and insure that there is no flow at the outlet of the pump.

10.2.2 Calculate the flow rate needed so that the canister(s) are pressurized to approximately one atmosphere above ambient pressure (2 atmospheres absolute pressure) over the desired sample period, utilizing the following equation:

$$F = \frac{(P)(V)(N)}{(T)(60)}$$

where:

F = flow rate (cm^3/min)

P = final canister pressure (atmospheres absolute) $= (P_g/P_a) + 1$

V = volume of the canister (cm^3)

N = number of canisters connected together for simultaneous sample collection

T = sample period (hours)

P_g = gauge pressure in canister, psig (kPa)

Pa = standard atmospheric pressure, 14.7 psig (101 kPa)

For example, if one 6-L canister is to be filled to 2 atmospheres absolute pressure (14.7 psig) in 3 hours, the flow rate would be calculated as follows:

$$F = \frac{2 \times 6000 \times 1}{3 \times 60} = 67\ cm^3/min$$

10.2.3 Select a critical orifice or hypodermic needle suitable to maintain a substantially constant flow at the calculated flow rate into the canister(s) over the desired sample period. A 30-gauge hypodermic needle, 2.5 cm long, provides a flow of approximately 65 cm^3/min with the Metal Bellows Model MBV-151 pump (see Figure 4). Such a needle will maintain approximately constant flow up to a canister pressure of about 10 psig (71 kPa), after which the flow drops with increasing pressure. At 14.7 psig (2 atmospheres absolute pressure), the flow is about 10% below the original flow.

10.2.4 Assemble the 2.0 micron stainless steel in-line particulate filter and position it in front of the critical orifice. A suggested filter-hypodermic needle assembly can be fabricated as illustrated in Figure 4.

10.2.5 Check the sampling system for contamination by filling two evacuated, cleaned canister(s) (See Section 10.1) with humidified zero air through the sampling system. Analyze the canisters according to Section 11.4. The sampling system is free of contamination if the canisters contain less than 0.02 ppmC hydrocarbons, similar to that of humidified zero air.

10.2.6 During the system contamination check procedure, check the critical orifice flow rate on the sampling system to insure that sample flow rate remains relatively constant (±10%) up to about 2 atmospheres absolute pressure (101 kPa). Note: A drop in the flow rate may occur near the end of the sampling period as the canister pressure approaches two atmospheres.

10.2.7 Reassemble the sampling system. If the inlet sample line is longer than 3 meters, install an auxiliary pump to ventilate the sample line, as illustrated in Figure 2.

10.2.8 Verify that the timer, pump(s) and solenoid valve are connected and operating properly.

10.2.9 Verify that the timer is correctly set for the desired sample period, and that the solenoid valve is closed.

10.2.10 Connect a cleaned, evacuated canister(s) (Section 10.1) to the non-contaminated sampling system, by way of the solenoid valve, for sample collection.

10.2.11 Make sure the solenoid valve is closed. Open the canister valve(s). Temporarily connect a small rotameter to the sample inlet to verify that there is no flow. Note: Flow detection would indicate a leaking (or open) solenoid valve. Remove the rotameter after leak detection procedure.

10.2.12 Fill out the necessary information on the Field Data Sheet (Figure 7).

10.2.13 Set the automatic timer to start and stop the pump or pumps to open and close the solenoid valve at the appropriate time for the intended sample period. Sampling will begin at the pre-determined time.

10.2.14 After the sample period, close the canister valve(s) and disconnect the canister(s) from the sampling system. Connect a pressure gauge to the canister(s) and briefly open and close the canister valve. Note the canister pressure on the Field Data Sheet (see Figure 7). The canister pressure should be approximately 2 atmospheres absolute [1 atmosphere or 101 kPa (gauge)]. Note: If the canister pressure is not approximately 2 atmospheres absolute (14.7 psig), determine and correct the cause before next sample. Re-cap canister valve.

10.2.15 Fill out the identification tag on the sample canister(s) and complete the Field Data Sheet as necessary. Note any activities or special conditions in the area (rain, smoke, etc.) that may affect the sample contents on the sampling data sheet.

10.2.16 Return the canister(s) to the analytical system for analysis.

11. Sample Analysis

11.1 Analytical System Leak Check

11.1.1 Before sample analysis, the analytical system is assembled (see Figure 1) and leak checked.

11.1.2 To leak check the analytical system, place the six-port gas valve in the trapping position. Disconnect and cap the absolute pressure gauge. Insert a pressure gauge capable of recording up to 60 psig at the vacuum valve outlet.

11.1.3 Attach a valve and a zero air supply to the sample inlet port. Pressurize the system to about 50 psig (350 kPa) and close the valve.

11.1.4 Wait approximately 3 hrs. and re-check pressure. If the pressure did not vary more than ± 2 psig, the system is considered leak tight.

11.1.5 If the system is leak free, de-pressurize and reconnect absolute pressure gauge.

11.1.6 The analytical system leak check procedure needs to be performed during the system checkout, during a series of analysis or if leaks are suspected. This should be part of the user-prepared SOP manual (see Section 12.1).

11.2 Sample Volume Determination

11.2.1 The vacuum reservoir and absolute pressure gauge are used to meter a precisely repeatable volume of sample air through the cryogenically-cooled trap, as follows: With the sample valve closed and the vacuum valve open, the reservoir is first evacuated with the vacuum pump to a predetermined pressure (e.g., 100 mm Hg). Then the vacuum valve is closed and the sample valve is opened to allow sample air to be drawn through the cryogenic trap and into the evacuated reservoir until a second predetermined reservoir pressure is reached (e.g., 300 mm Hg). The (fixed) volume of air thus sampled is determined by the pressure rise in the vacuum reservoir (difference between the predetermined pressures) as measured by the absolute pressure gauge (see Section 12.2.1).

11.2.2 The sample volume can be calculated by:

$$V_s = \frac{(\Delta P)(V_r)}{(P_s)}$$

where:

V_s = volume of air sampled (standard cm^3)

ΔP = pressure difference measured by gauge (mm Hg)

V_r = volume of vacuum reservoir (cm^3) usually 1 L

P_s = standard pressure (760 mm Hg)

For example, with a vacuum reservoir of 1000 cm^3 and a pressure change of 200 mm Hg (100 to 300 mm Hg), the volume sampled would be 263 cm^3. [Note: Typical sample volume using this procedure is between 200-300 cm^3.]

11.2.3 The sample volume determination need only be performed once during the system check-out and shall be part of the user-prepared SOP Manual (see Section 12.1).

11.3 Analytical System Dynamic Calibration

11.3.1 Before sample analysis, a complete dynamic calibration of the analytical system should be carried out at five or more concentrations on each range to define the calibration curve. This should be carried out initially and periodically thereafter [may be done only once during a series of analyses]. This should be part of the user-prepared SOP Manual (See Section 12.1). The calibration should be verified with two or three-point calibration checks (including zero) each day the analytical system is used to analyze samples.

11.3.2 Concentration standards of propane are used to calibrate the analytical system. Propane calibration standards may be obtained directly from low concentration cylinder standards or by dilution of high concentration cylinder standards with zero air (see Section 8.3). Dilution flow rates must be measured accurately, and the combined gas stream must be mixed thoroughly for successful calibration of the analyzer. Calibration standards should be sampled directly from a vented manifold or tee. Note: Remember that a propane NMOC concentration in ppmC is three times the volumetric concentration in ppm.

11.3.3 Select one or more combinations of the following parameters to provide the desired range or ranges (e.g., 0-1.0 ppmC or 0-5.0 ppmC): FID attenuator setting, output voltage setting, integrator resolution (if applicable), and sample volume. Each individual range should be calibrated separately and should have a separate calibration curve. Note: Modern GC integrators may provide automatic ranging such that several decades of concentration may be covered in a single range. The user-prepared SOP manual should address variations applicable to a specific system design (see Section 12.1).

11.3.4 Analyze each calibration standard three times according to the procedure in Section 11.4. Insure that flow rates, pressure gauge start and stop readings, initial cryogen liquid level in the Dewar, timing, heating, integrator settings, and other variables are the same as those that will be used during analysis of ambient samples. Typical flow rates for the gases are: hydrogen, 30 cm^3/minute; helium carrier, 30 cm^3/minute; burner air, 400 cm^3/minute.

11.3.5 Average the three analyses for each concentration standard and plot the calibration curve(s) as average integrated peak area reading versus concentration in ppmC. The relative standard deviation for the three analyses should be less than 3% (except for zero concentration). Linearity should be expected; points that appear to deviate abnormally should be repeated. Response has been shown to be linear over a wide range (0-10,000 ppbC). If nonlinearity is observed, an effort should be made to identify and correct the problem. If the problem cannot be corrected, additional points in the nonlinear region may be needed to define the calibration curve adequately.

11.4 Analysis Procedure

11.4.1 Insure the analytical system has been assembled properly, leaked checked, and properly calibrated through a dynamic standard calibration. Light the FID detector and allow to stabilize.

11.4.2 Check and adjust the helium carrier pressure to provide the correct carrier flow rate for the system. Helium is used to purge residual air and methane from the trap at the end of the sampling phase and to carry the re-volatilized NMOC from the trap into the FID. A single-stage auxiliary regulator between the cylinder and the analyzer may not be necessary, but is recommended to regulate the helium pressure better than the multistage cylinder regulator. When an auxiliary regulator is used, the secondary stage of the two-stage regulator must be set at a pressure higher than the pressure setting of the single-stage regulator. Also check the FID hydrogen and burner air flow rates (see 11.3.4).

11.4.3 Close the sample valve and open the vacuum valve to evacuate the vacuum reservoir to a specific predetermined value (e.g., 100 mm Hg).

11.4.4 With the trap at room temperature, place the six-port valve in the inject position.

11.4.5 Open the sample valve and adjust the sample flow rate needle valve for an appropriate trap flow of 50-100 cm^3/min. Note: The flow will be lower later, when the trap is cold.

11.4.6 Check the sample canister pressure before attaching it to the analytical system and record on Field Data Sheet (see Figure 7). Connect the sample canister or direct sample inlet to the six-port valve, as shown in Figure 1. For a canister, either the canister valve or an optional fine needle valve installed between the canister and the vent is used to adjust the canister flow rate to a value slightly higher than the trap flow rate set by the sample flow rate needle valve. The excess flow exhausts through the vent, which assures that the sample air flowing through the trap is at atmospheric pressure. The vent is connected to a flow indicator such as a rotameter as an indication of vent flow to assist in adjusting the flow control valve. Open the canister valve and adjust the canister valve or the sample flow needle valve to obtain a moderate vent flow as indicated by the rotameter. The sample flow rate will be lower (and hence the vent flow rate will be higher) when the the trap is cold.

11.4.7 Close the sample valve and open the vacuum valve (if not already open) to evacuate the vacuum reservoir. With the six-port valve in the inject position and the vacuum valve open, open the sample valve for 2-3 minutes [with both valves open, the pressure reading won't change] to flush and condition the inlet lines.

11.4.8 Close the sample valve and evacuate the reservoir to the predetermined sample starting pressure (typically 100 mm Hg) as indicated by the absolute pressure gauge.

11.4.9 Switch the six-port valve to the sample position.

11.4.10 Submerge the trap in the cryogen. Allow a few minutes for the trap to cool completely (indicated when the cryogen stops boiling). Add cryogen to the initial level used during system dynamic calibration. The level of the cryogenic liquid should remain constant with respect to the trap and should completely cover the beaded portion of the trap.

11.4.11 Open the sample valve and observe the increasing pressure on the pressure gauge. When it reaches the specific predetermined pressure (typically 300 mm Hg) representative of the desired sample volume (Section 11.2), close the sample valve.

11.4.12 Add a little cryogen or elevate the Dewar to raise the liquid level to a point slightly higher (3-15 mm) than the initial level at the beginning of the trapping. Note: This insures that organics do not bleed from the trap and are counted as part of the NMOC peak(s).

11.4.13 Switch the 6-port valve to the inject position, keeping the cryogenic liquid on the trap until the methane and upset peaks have deminished (10-20 seconds). Now close the canister valve to conserve the remaining sample in the canister.

11.4.14 Start the integrator and remove the Dewar flask containing the cryogenic liquid from the trap.

11.4.15 Close the GC oven door and allow the GC oven (or alternate trap heating system) to heat the trap at a predetermined rate (typically, 30°C/min) to 90°. Heating the trap volatilizes the concentrated NMOC such that the FID produces integrated peaks. A uniform trap temperature rise rate (above 0°C) helps to reduce variability and facilitates more accurate correction for the moisture-shifted baseline. With a chromatograph oven to heat the trap, the following parameters have been found to be acceptable: initial temperature, 30°C; initial time, 0.20 minutes (following start of the integrator); heat rate, 30°/minute; final temperature, 90°C.

11.4.16 Use the same heating process and temperatures for both calibration and sample analysis. Heating the trap too quickly may cause an initial negative response that could hamper accurate integration. Some initial experimentation may be necessary to determine the optimal heating procedure for each system. Once established, the procedure should be consistent for each analysis as outlined in the user-prepared SOP Manual.

11.4.17 Continue the integration (generally, in the range of 1-2 minutes is adequate) only long enough to include all of the organic compound peaks and to establish the end point FID baseline, as illustrated in Figure 8. The integrator should be capable of marking the beginning and ending of peaks, constructing the appropriate operational baseline between the start and end of the integration period, and calculating the resulting corrected peak area. This ability is necessary because the moisture in the sample, which is also concentrated in the trap, will cause a slight positive baseline shift. This baseline shift starts as the trap warms and continues until all of the moisture is swept from the trap, at which time the baseline returns to its normal level. The shift always continues longer than the ambient organic peak(s). The integrator should be programmed to correct for this shifted baseline by ending the integration at a point after the last NMOC peak and prior to the return of the shifted baseline to normal (see Figure 8) so that the calculated operational baseline effectively compensates for the water-shifted baseline. Electronic integrators either do this automatically or they should be programmed to make this correction. Alternatively, analyses of humidified zero air prior to sample analyses should be performed to determine the water envelope and the proper blank value for correcting the ambient air concentration measurements accordingly. Heating and flushing of the trap should continue after the integration period has ended to insure all water has been removed to prevent buildup of water in the trap. Therefore, be sure that the 6-port valve remains in the inject position until all moisture has purged from the trap (3 minutes or longer).

11.4.18 Use the dynamic calibration curve (see Section 11.3) to convert the integrated peak area reading into concentration units (ppmC). Note that the NMOC peak shape may not be precisely reproducible due to variations in heating the trap, but the total NMOC peak area should be reproducible.

11.4.19 Analyze each canister sample at least twice and report the average NMOC concentration. Problems during an analysis occasionally will cause erratic or inconsistent results. If the first two analyses do not agree within ± 5% relative standard deviation (RSD), additional analyses should be made to identify inaccurate measurements and produce a more accurate average (see also Section 12.2.).

12. Performance Criteria and Quality Assurance

This section summarizes required quality assurance measures and provides guidance concerning performance criteria that should be achieved within each laboratory.

12.1 Standard Operating Procedures (SOPs)

12.1.1 Users should generate SOPs describing and documenting the following activities in their laboratory: (1) assembly, calibration, leak check, and operation of the specific sampling system and equipment used; (2) preparation, storage, shipment, and handling of samples; (3) assembly, leak-check, calibration, and operation of the analytical system, addressing the specific equipment used; (4) canister storage and cleaning; and (5) all aspects of of data recording and processing, including lists of computer hardware and software used.

12.1.2 SOPs should provide specific stepwise instructions and should be readily available to, and understood by, the laboratory personnel conducting the work.

12.2 Method Sensitivity, Accuracy, Precision and Linearity

12.2.1 The sensitivity and precision of the method is proportional to the sample volume. However, ice formation in the trap may reduce or stop the sample flow during trapping if the sample volume exceeds 500 cm^3. Sample volumes below about 100-150 cm^3 may cause increased measurement variability due to dead volume in lines and valves. For most typical ambient NMOC concentrations, sample volumes in the range of 200-400 cm^3 appear to be appropriate. If a response peak obtained with a 400 cm^3 sample is off scale or exceeds the calibration range, a second analysis can be carried out with a smaller volume. The actual sample volume used need not be accurately known if it is precisely repeatable during both calibration and analysis. Similarly, the actual volume of the vacuum reservoir need not be accurately known. But the reservoir volume should be matched to the pressure range and resolution of the absolute pressure gauge so that the measurement of the pressure change in the reservoir, hence the sample volume, is repeatable within 1%. A 1000 cm^3 vacuum reservoir and a pressure change of 200 mm Hg, measured with the specified pressure gauge, have provided a sampling precision of $\pm$ 1.31 cm^3. A smaller volume reservoir may be used with a greater pressure change to accommodate absolute pressure gauges with lower resolution, and vice versa.

12.2.2 Some FID detector systems associated with laboratory chromatographs may have autoranging. Others may provide attenuator control and internal full-scale output voltage selectors. An appropriate combination should be chosen so that an adequate output level for accurate integration is obtained down to the detection limit; however, the electrometer or integrator must not be driven into saturation at the upper end of the calibration. Saturation of the electrometer may be indicated by flattening of the calibration curve at high concentrations. Additional adjustments of range and sensitivity can be provided by adjusting the sample volume used, as discussed in Section 12.2.1.

12.2.3 System linearity has been documented (6) from 0 to 10,000 ppbC.

12.2.4 Some organic compounds contained in ambient air are "sticky" and may require repeated analyses before they fully appear in the FID output. Also, some adjustment may have to be made in the integrator off time setting to accommodate compounds that reach the FID late in the analysis cycle. Similarly, "sticky" compounds from ambient samples or from contaminated propane standards may temporarily contaminate the analytical system and can affect subsequent analyses. Such temporary contamination can usually be removed by repeated analyses of humidified zero air.

12.2.5 Simultaneous collection of duplicate samples decreases the possibility of lost measurement data from samples lost due to leakage or contamination in either of the canisters. Two (or more) canisters can be filled simultaneously by connecting them in parallel (see Figure 2(a)) and selecting an appropriate flow rate to accommodate the number of canisters (Section 10.2.2). Duplicate (or replicate) samples also allow assessment of measurement precision based on the differences between duplicate samples (or the standard deviations among replicate samples).

13. Method Modification

13.1 Sample Metering System

13.1.1 Although the vacuum reservoir and absolute pressure gauge technique for metering the sample volume during analysis is efficient and convenient, other techniques should work also.

13.1.2 A constant sample flow could be established with a vacuum pump and a critical orifice, with the six-port valve being switched to the sample position for a measured time period.

A gas volume meter, such as a wet test meter, could also be used to measure the total volume of sample air drawn through the trap. These alternative techniques should be tested and evaluated as part of a user-prepared SOP manual.

13.2 FID Detector System

13.2.1 A variety of FID detector systems should be adaptable to the method.

13.2.2 The specific flow rates and necessary modifications for the helium carrier for any alternative FID instrument should be evaluated prior to use as part of the user-prepared SOP manual.

13.3 Range

13.3.1 It may be possible to increase the sensitivity of the method by increasing the sample volume. However, limitations may arise such as plugging of the trap by ice.

13.3.2 Any attempt to increase sensitivity should be evaluated as part of the user-prepared SOP manual.

13.4 Sub-Atmospheric Pressure Canister Sampling

13.4.1 Collection and analysis of canister air samples at sub-atmospheric pressure is also possible with minor modifications to the sampling and analytical procedures.

13.4.2 Method TO-14, "Integrated Canister Sampling for Selective Organics: Pressurized and Sub-atmospheric Collection Mechanism," addresses sub-atmospheric pressure canister sampling. Additional information can be found in the literature (11-17).

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14. McClenny, W. A. Pleil J.D. Holdren, J.W.; and Smith, R.N.; 1984. " Automated Cryogenic Preconcentration and Gas Chromatographic Determination of Volatile Organic Compounds," Anal. Chem. 56:2947.

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16. Oliver, K. D.; Pleil, and McClenny, W. A.; 1986. "Sample Integrity of Trace Level Volatile Organic Compounds in Ambient Air Stored in Summa® Polished Canisters," Atmospheric Environ. 20:1403.

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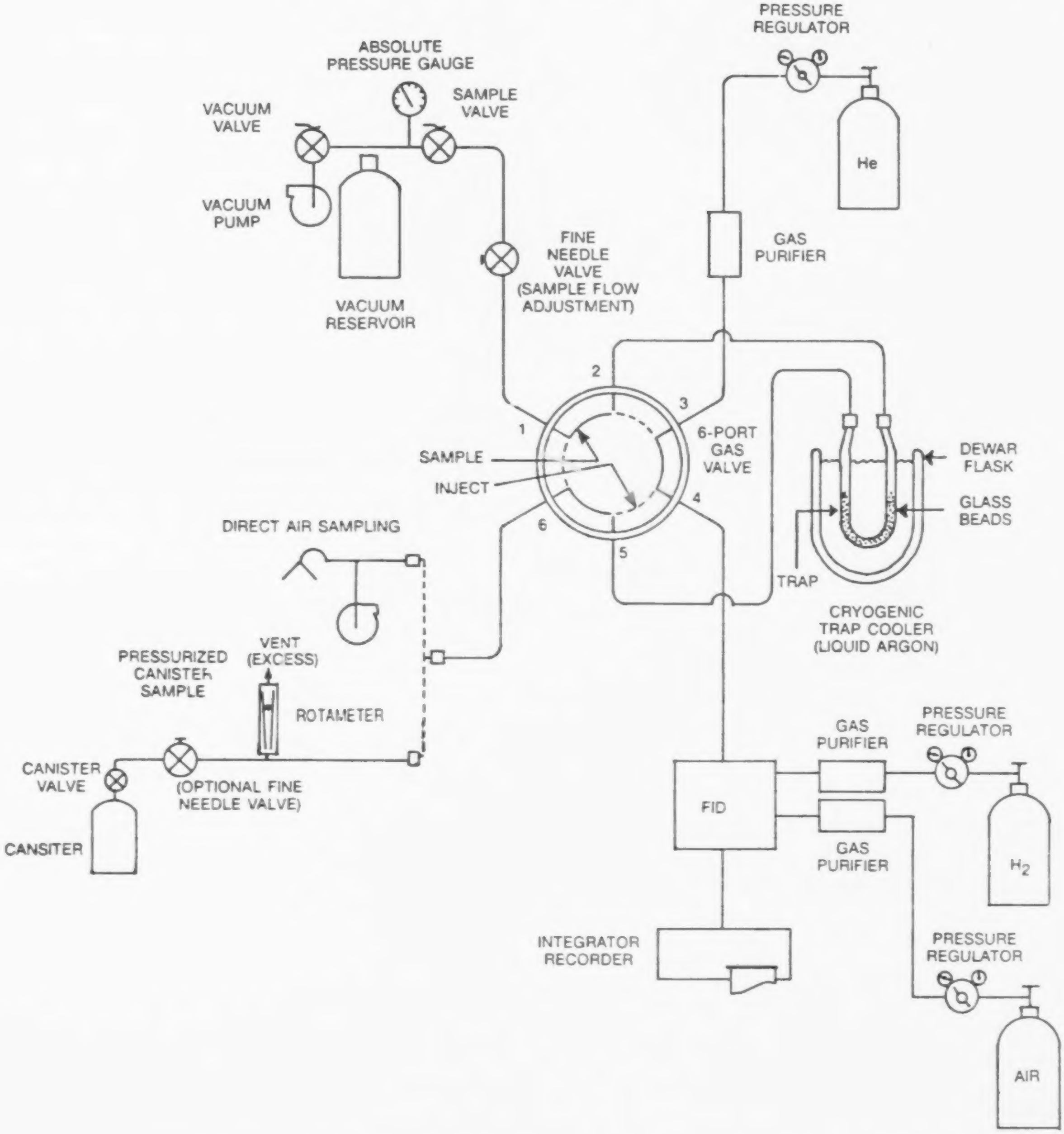

PRESSURE REGULATOR
ABSOLUTE PRESSURE GAUGE
VACUUM VALVE
SAMPLE VALVE
He
VACUUM PUMP
FINE NEEDLE VALVE (SAMPLE FLOW ADJUSTMENT)
GAS PURIFIER
VACUUM RESERVOIR
2
3
1
6-PORT GAS VALVE
DEWAR FLASK
SAMPLE
INJECT
GLASS BEADS
4
DIRECT AIR SAMPLING
6
5
TRAP
CRYOGENIC TRAP COOLER (LIQUID ARGON)
PRESSURIZED CANISTER SAMPLE
VENT (EXCESS)
ROTAMETER
GAS PURIFIER
PRESSURE REGULATOR
CANISTER VALVE
(OPTIONAL FINE NEEDLE VALVE)
FID
CANSITER
GAS PURIFIER
H_2
INTEGRATOR RECORDER
PRESSURE REGULATOR
AIR

FIGURE 1. SCHEMATIC OF ANALYTICAL SYSTEM FOR NMOC—TWO SAMPLING MODES

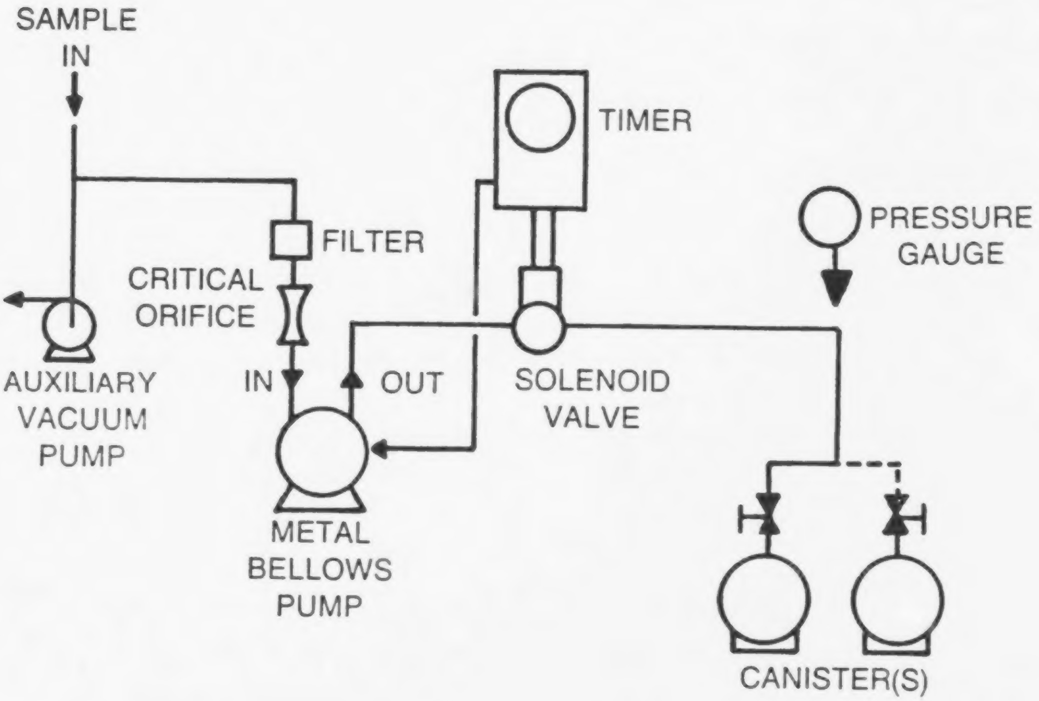
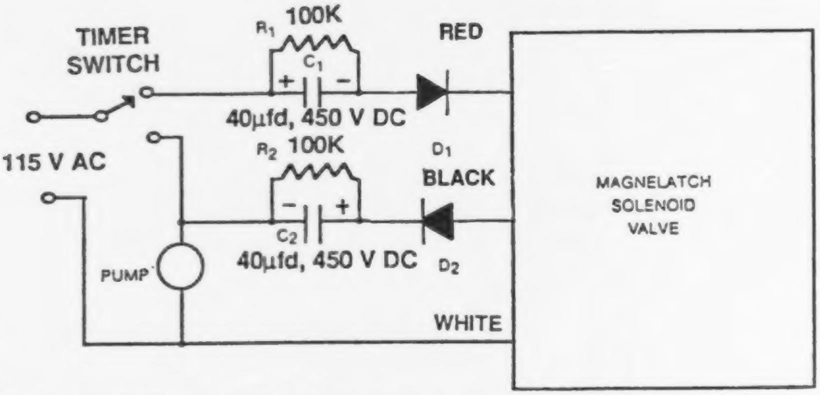

SAMPLE IN
TIMER
FILTER
PRESSURE GAUGE
CRITICAL ORIFICE
AUXILIARY VACUUM PUMP
IN
OUT
SOLENOID VALVE
METAL BELLOWS PUMP
CANISTER(S)

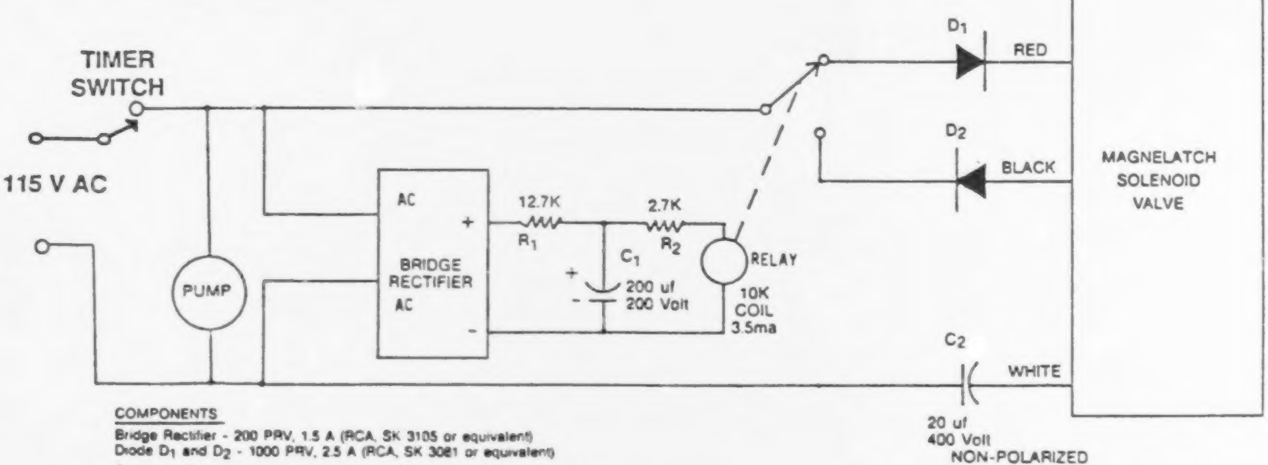
FIGURE 2. SAMPLE SYSTEM FOR AUTOMATIC COLLECTION OF 3-HOUR INTEGRATED AIR SAMPLES


TIMER SWITCH
115 V AC
R1 100K
C1
+
−
40µfd, 450 V DC
R2 100K
−
+
C2
40µfd, 450 V DC
RED
D1
BLACK
D2
WHITE
PUMP
MAGNELATCH SOLENOID VALVE

COMPONENTS

Capacitor C_1 and C_2 - 40 uf, 450 VDC (Sprague Atom® TVA 1712 or equivalent)
Resister R_1 and R_2 - 0.5 watt, 5% tolerance
Diode D_1 and D_2 - 1000 PRV, 2.5 A (RCA, SK 3081 or equivalent)

FIGURE 3[a]. SIMPLE CIRCUIT FOR OPERATING MAGNELATCH VALVE


TIMER SWITCH
115 V AC
PUMP
AC
+
BRIDGE RECTIFIER
AC
−
12.7K
R1
+
−
C1
200 uf
200 Volt
2.7K
R2
RELAY
10K COIL 3.5ma
D1
RED
D2
BLACK
C2
WHITE
20 uf
400 Volt
NON-POLARIZED
MAGNELATCH SOLENOID VALVE

COMPONENTS

Bridge Rectifier - 200 PRV, 1.5 A (RCA, SK 3105 or equivalent)
Diode D_1 and D_2 - 1000 PRV, 2.5 A (RCA, SK 3081 or equivalent)
Capacitor C_1 - 200 uf, 250 VDC (Sprague Atom® TVA 1528 or equivalent)
Capacitor C_2 - 20 uf, 400 VDC Non-Polarized (Sprague Atom® TVAN 1652 or equivalent)
Relay - 10,000 ohm coil, 3.5 ma (AMF Potter and Brumfield, KCP 5, or equivalent)
Resister R_1 and R_2 - 0.5 watt, 5% tolerance

FIGURE 3[b]. IMPROVED CIRCUIT DESIGNED TO HANDLE POWER INTERRUPTIONS

FIGURE 3. ELECTRICAL PULSE CIRCUITS FOR DRIVING SKINNER MAGNELATCH SOLENOID VALVE WITH A MECHANICAL TIMER

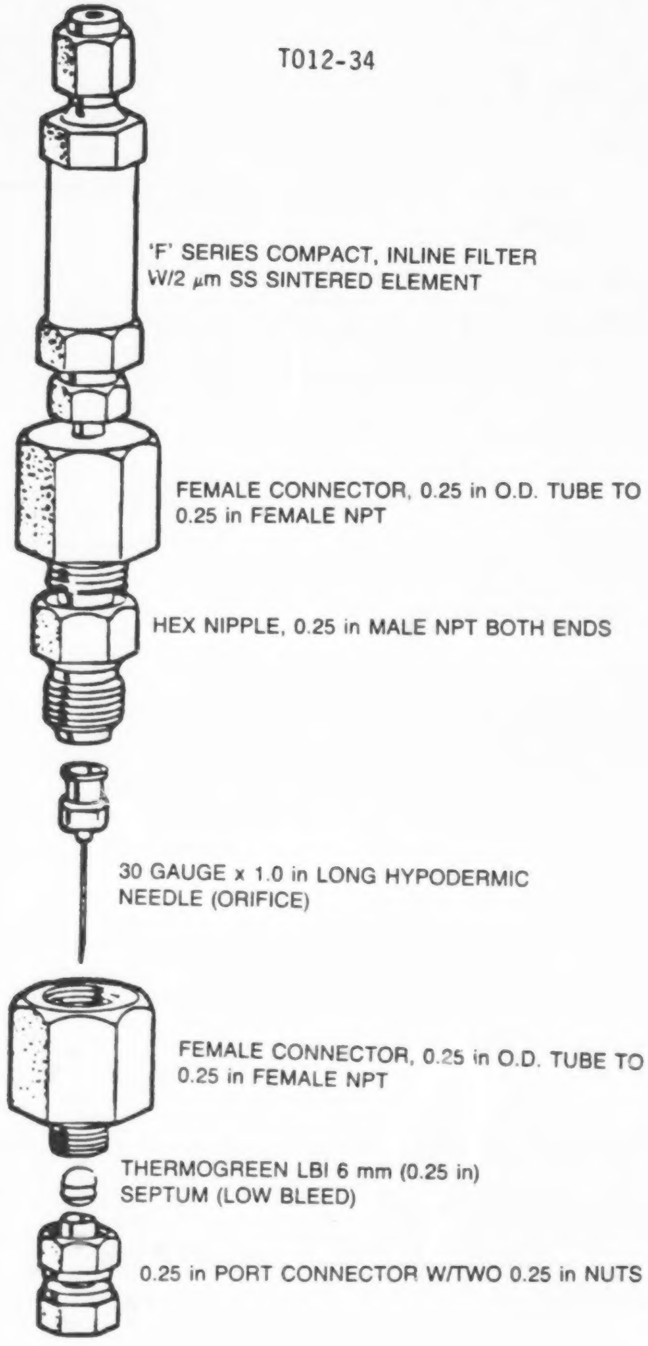

'F' SERIES COMPACT, INLINE FILTER
W/2 μm SS SINTERED ELEMENT
FEMALE CONNECTOR, 0.25 in O.D. TUBE TO
0.25 in FEMALE NPT
HEX NIPPLE, 0.25 in MALE NPT BOTH ENDS
30 GAUGE x 1.0 in LONG HYPODERMIC
NEEDLE (ORIFICE)
FEMALE CONNECTOR, 0.25 in O.D. TUBE TO
0.25 in FEMALE NPT
THERMOGREEN LBI 6 mm (0.25 in)
SEPTUM (LOW BLEED)
0.25 in PORT CONNECTOR W/TWO 0.25 in NUTS

FIGURE 4. FILTER AND HYPODERMIC NEEDLE ASSEMBLY FOR SAMPLE INLET FLOW CONTROL

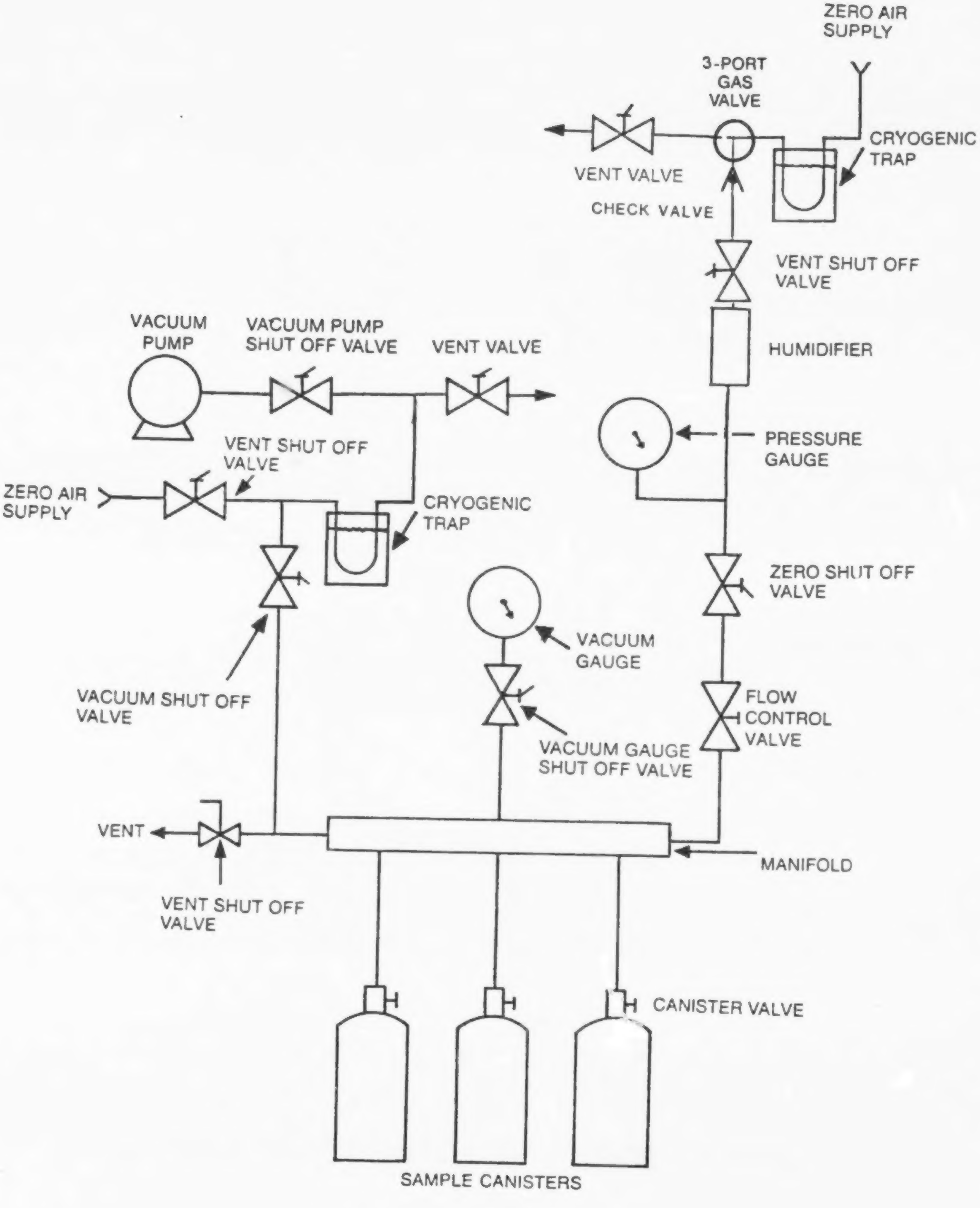

ZERO AIR SUPPLY
3-PORT GAS VALVE
CRYOGENIC TRAP
VENT VALVE
CHECK VALVE
VENT SHUT OFF VALVE
HUMIDIFIER
PRESSURE GAUGE
VACUUM PUMP
VACUUM PUMP SHUT OFF VALVE
VENT VALVE
VENT SHUT OFF VALVE
ZERO AIR SUPPLY
CRYOGENIC TRAP
ZERO SHUT OFF VALVE
VACUUM GAUGE
VACUUM SHUT OFF VALVE
FLOW CONTROL VALVE
VACUUM GAUGE SHUT OFF VALVE
VENT
MANIFOLD
VENT SHUT OFF VALVE
CANISTER VALVE
SAMPLE CANISTERS

FIGURE 5. CANISTER CLEANING SYSTEM

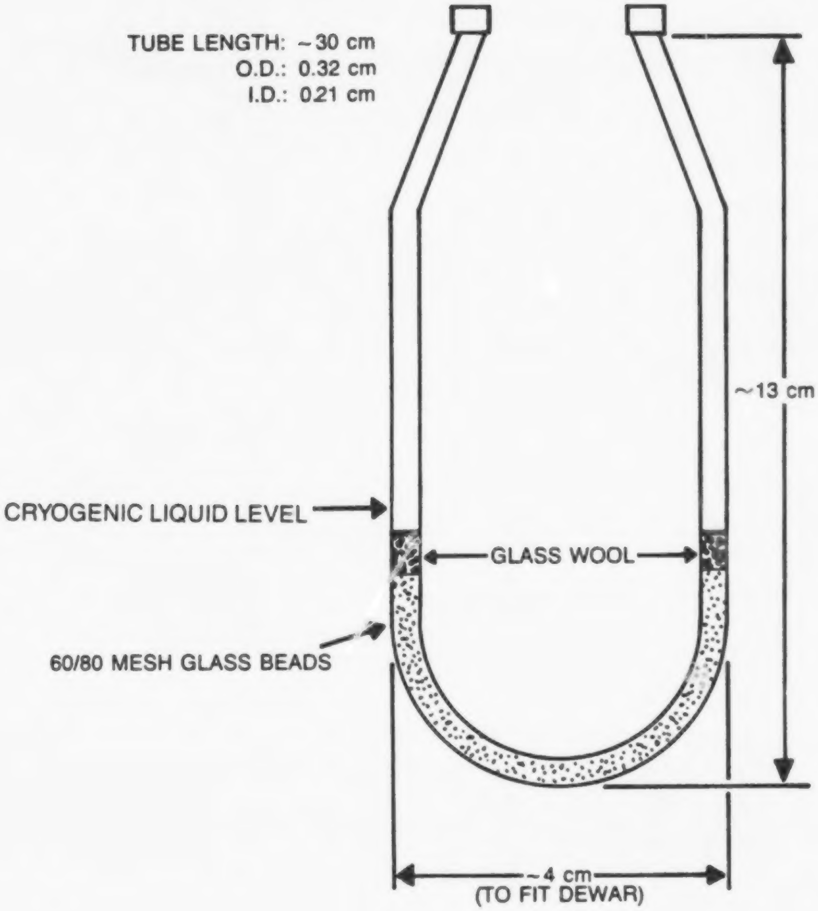

TUBE LENGTH: ~30 cm
O.D.: 0.32 cm
I.D.: 0.21 cm
CRYOGENIC LIQUID LEVEL
GLASS WOOL
60/80 MESH GLASS BEADS
~13 cm
~4 cm
(TO FIT DEWAR)

FIGURE 6. CRYOGENIC SAMPLE TRAP DIMENSIONS

PRESSURIZED CANISTER SAMPLING DATA SHEET

GENERAL INFORMATION:

PROJECT: ____________________
SITE: ____________________
LOCATION: ____________________
MONITOR STATION NUMBER: ____________________
PUMP SERIAL NUMBER: ____________________

OPERATOR: ____________________
ORIFICE IDENTIFICATION: ____________________
FLOW RATE: ____________________
CALIBRATED BY: ____________________
LEAK CHECK ________ Pass ________ Fail

FIELD DATA:

Date	Canister Serial Number	Sample Number	Sample Time		Average Atmospheric Conditions			Canister pressure Final, Laboratory		Comments
			Start	Stop	Temperature	Pressure	Relative Humidity			

Date ____________________ Title ____________________ Signature ____________________

FIGURE 7. EXAMPLE SAMPLING DATA SHEET

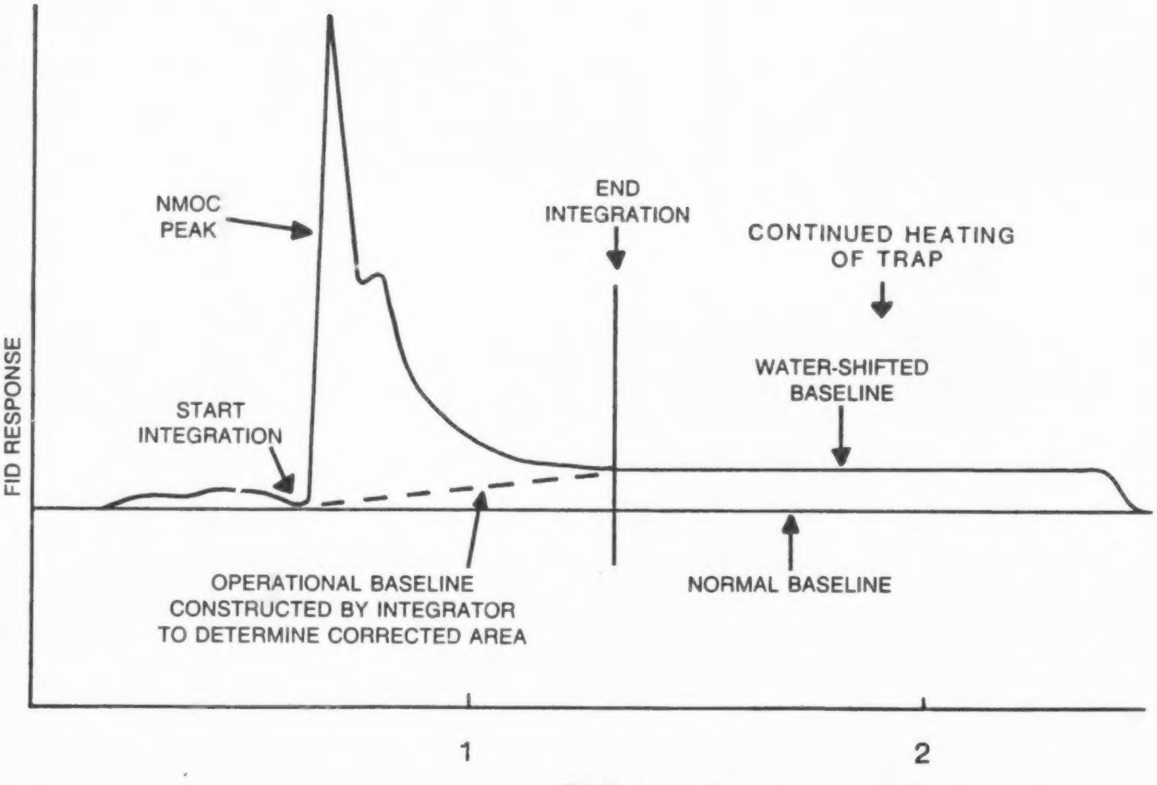


FIGURE 8. **CONSTRUCTION OF OPERATIONAL BASELINE AND CORRESPONDING CORRECTION OF PEAK AREA**

Revision 1.0
June, 1988

METHOD TO-13

THE DETERMINATION OF BENZO(a)PYRENE [B(a)P] AND OTHER POLYNUCLEAR AROMATIC HYDROCARBONS (PAH's) IN AMBIENT AIR USING GAS CHROMATOGRAPHIC (GC) AND HIGH PERFORMANCE LIQUID CHROMATOGRAPHIC (HPLC) ANALYSIS

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        12.4.2 Lobar Prepacked Column Procedure

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        13.4.2 Internal Standard Calibration Procedure
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        14.3.2 Internal Standard Calibration
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        14.4.4 Analyte Identification
        14.4.5 Spectrum Comparison
        14.4.6 Analyte Quantification
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        15.4.3 Replacement of Stock Standard Solution
        15.4.4 Calibration Standards
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    16.2 Process, Field and Solvent Blanks
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    16.5 High Performance Liquid Chromatography Detection

OUTLINE (cont'd)

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    - 17.2 Sample Concentration
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        - 17.2.2 Gas Chromatography with Mass Spectroscopy Detection
        - 17.2.3 High Performance Liquid Chromatography Detection
    - 17.3 Sample Conversion from ng/m^3 to ppbv

18. Bibliography

METHOD TO-13

THE DETERMINATION OF BENZO(a)PYRENE [B(a)P] AND OTHER POLYNUCLEAR AROMATIC HYDROCARBONS (PAHs) IN AMBIENT AIR USING GAS CHROMATOGRAPHIC (GC) AND HIGH PERFORMANCE LIQUID CHROMATOGRAPHIC (HPLC) ANALYSIS

1. Scope

1.1 Polynuclear aromatic hydrocarbons (PAHs) have received increased attention in recent years in air pollution studies because some of these compounds are highly carcinogenic or mutagenic. In particular, benzo[a]pyrene (B[a]P) has been identified as being highly carcinogenic. To understand the extent of human exposure to B[a]P, and other PAHs, a reliable sampling and analytical method has been established. This document describes a sampling and analysis procedure for B[a]P and other PAHs involving a combination quartz filter/adsorbent cartridge with subsequent analysis by gas chromatography (GC) with flame ionization (FI) and mass spectrometry (MS) detection (GC/FI and GC/MS) or high resolution liquid chromatography (HPLC). The analytical methods are a modification of EPA Test Method 610 and 625, Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater, and Methods 8000, 8270, and 8310, Test Methods for Evaluation of Solid Waste.

1.2 Fluorescence methods were among the very first methods used for detection of B[a]P and other PAHs as a carcinogenic constituent of coal tar (1-7). Fluorescent methods are capable of measuring subnanogram quantities of PAHs, but tend to be fairly non-selective. The normal spectra obtained tended to be intense and lacked resolution. Efforts to overcome this difficulty led to the use of ultraviolet (UV) absorption spectroscopy as the detection method coupled with pre-speciated techniques involving liquid chromatography (LC) and thin layer chromatography (TLC) to isolate specific PAHs, particularly B[a]P (8). As with fluorescence spectroscopy, the individual spectra for various PAHs are unique, although portions of spectra for different compounds may be the same. As with fluoresence techniques, the possibility of spectra overlap required complete separation of sample components to insure accurate measurement of component levels. Hence, the use of UV absorption coupled with pre-speciation involving LC and TLC and fluorescence spectroscopy has declined and is now being replaced with the more sensitive high performance liquid chromatography (9) with UV/fluorescence detection and highly sensitive and specific gas chromatograph with either flame ionization detector or coupled with mass spectroscopy (10-11).

1.3 The choice of GC and HPLC as the recommended procedures for analysis of B[a]P and other PAHs are influenced by their sensitivity and selectivity, along with their ability to analyze complex samples. This method provides for both GC and HPLC approaches to the determination of B[a]P and other PAHs in the extracted sample.

1.4 The analytical methodology is well defined, but the sampling procedures can reduce the validity of the analytical results. Recent studies (12-15) have indicated that non-volatile PAHs (vapor pressure $<10^{-8}$ mm Hg) may be trapped on the filter, but post-collection volatilization problems may distribute the PAHs down stream of the the filter to the back-up adsorbent. A wide variety of adsorbents such as Tenax GC, XAD-2 resin and polyurethane foam (PUF) have been used to sample B[a]P and other PAH vapors. All adsorbents have demonstrated high collection efficiency for B[a]P in particular. In general, XAD-2 resin has a higher collection efficiency (16-17) for volatile PAHs than PUF, as well as a higher retention efficiency. However, PUF cartridges are easier to handle in the field and maintain better flow characteristics during sampling. Likewise, PUF has demonstrated its capability in sampling organochlorine pesticides and polychlorinated biphenyls (Compendium Methods T04 and T010 respectively), and polychlorinated dibenzo-p-dioxins (Compendium Method T09). However, PUF has demonstrated a lower recovery efficiency and storage capability for naphthalene and B[a]P, respectively, than XAD-2. There have been no significant losses of PAHs, up to 30 days of storage at 0°C, using XAD-2. It also appears that XAD-2 resin has a higher collection efficiency for volatile PAHs than PUF, as well as a higher retention efficiency for both volatile and reactive PAHs. Consequently, while the literature cites weaknesses and strengths of using either XAD-2 or PUF, this method covers both the utilization of XAD-2 and PUF as the adsorbent to address post-collection volatilization problems associated with B[a]P and other reactive PAHs.

1.5 This method covers the determination of B[a]P specificially by both GC and HPLC and enables the qualitative and quantitative analysis of the other PAHs. They are:

Acenaphthene
Acenaphthylene
Anthracene
Benzo(a)anthracene
Benzo(a)pyrene
Benzo(b)fluoranthene
Benzo(e)pyrene
Benzo(g,h,i)perylene
Benzo(k)fluoranthene
Chrysene
Dibenzo(a,h)anthracene
Fluoranthene
Fluorene
Indeno(1,2,3-cd)pyrene
Naphthalene
Phenanthrene
Pyrene

The GC and HPLC methods are applicable to the determination of PAHs compounds involving two-member rings or higher. Nitro-PAHs have not been fully evaluated using this procedure; therefore, they are not included in this method. When either of the methods are used to analyze unfamiliar samples for any or all of the compounds listed above, compound identification should be supported by both techniques.

1.6 With careful attention to reagent purity and optimized analytical conditions, the detection limits for GC and HPLC methods range from 1 ng to 10 pg which represents detection of B[a]P and other PAHs in filtered air at levels below 100 pg/m^3. To obtain this detection limit, at least 100 m^3 of air must be sampled.

2. Applicable Documents

2.1 ASTM Standards

2.1.1 Method D1356 - Definitions of Terms Relating to Atmospheric Sampling and Analysis.

2.1.2 Method E260 - Recommended Practice for General Gas Chromatography Procedures.

2.1.3 Method E355 - Practice for Gas Chromatography Terms and Relationships.

2.1.4 Method E682 - Practice for Liquid Chromatography Terms and Relationships.

2.1.5 Method D-1605-60 - Standard Recommended Practices for Sampling Atmospheres for Analysis of Gases and Vapors.

2.2 Other Documents

2.2.1 Existing Procedures (18-25)

2.2.2 Ambient Air Studies (26-28)

2.2.3 U.S. EPA Technical Assistance Document (29-32)

2.2.4 General Metal Works Operating Procedures for Model PS-1 Sampler, General Metal Works, Inc., Village of Cleves, Ohio.

3. Summary of Method

3.1 Filters and adsorbent cartridges (containing XAD-2 or PUF) are cleaned in solvents and vacuum-dried. The filters and adsorbent cartridges are stored in screw-capped jars wrapped in aluminum foil (or otherwise protected from light) before careful installation on a modified high volume sampler.

3.2 Approximately 325 m^3 of ambient air is drawn through the filter and adsorbent cartridge using a calibrated General Metal Works Model PS-1 Sampler, or equivalent (breakthrough has not shown to be a problem with sampling volumes of 325 m^3).

3.3 The amount of air sampled through the filter and adsorbent cartridge is recorded, and the filter and cartridge are placed in an appropriately labeled container and shipped along with blank filter and adsorbent cartridges to the analytical laboratory for analysis.

3.4 The filters and adsorbent cartridge are extracted by Soxhlet extraction with appropriate solvent. The extract is concentrated by Kuderna-Danish (K-D) evaporator, followed by silica gel clean-up using column chromatography to remove potential interferences prior to analysis.

3.5 The eluent is further concentrated by K-D evaporator, then analyzed by either gas chromatograhy equipped with FI or MS detection or high performance liquid chromatography (HPLC). The analytical system is verified to be operating properly and calibrated with five concentration calibration solutions, each analyzed in triplicate.

3.6 A preliminary analysis of the sample extract is performed to check the system performance and to ensure that the samples are within the calibration range of the instrument. If necessary, recalibrate the instrument, adjust the amount of the sample injected, adjust the calibration solution concentration, and adjust the data processing system to reflect observed retention times, etc.

3.7 The samples and the blanks are analyzed and used (along with the amount of air sampled) to calculated the concentratuon of B[a]P in ambient air.

3.8 Other PAHs can be determined both qualitatively and quantitatively through optimization of the GC or HPLC procedures.

4. Significance

4.1 Several documents have been published which describe sampling and analytical approaches for benzo[a]pyrene and other PAHs, as outlined in Section 2.2. The attractive features of these methods have been combined in this procedure. This method has been validated in the laboratory; however, one must use caution when employing it for specific applications.

4.2 The relatively low level of B[a]P and other PAHs in the environment requires use of high volume ($\sim$6.7 cfm) sampling techniques to acquire sufficient sample for analysis. However, the volatility of certain PAHs prevents efficient collection on filter media alone. Consequently, this method utilizes both a filter and a backup adsorbent cartridge which provide for efficient collection of most PAHs.

5. Definitions

Definitions used in this document and in any user-prepared standard operating procedures (SOPs) should be consistent with ASTM Methods D1356, D1605-60, E260, and E255. All abbreviations and symbols are defined within this document at point of use.

5.1 Sampling efficiency (SE) - ability of the sampling medium to trap vapors of interest. %SE is the percentage of the analyte of interest colleted and retained by the sampling medium when it is introduced as a vapor in air or nitrogen into the air sampler and the sampler is operated under normal conditions for a period of time equal to or greater than that required for the intended use.

5.2 Retention time (RT) - time to elute a specific chemical from a chromatographic column. For a specific carrier gas flow rate, RT is measured from the time the chemical is injected into the gas stream until it appears at the detector.

5.3 High Performance Liquid Chromatography - an analytical method based on separation of compounds of a liquid mixture through a liquid chromatographic column and measuring the separated components with a suitable detector.

5.4 Gradient elution - defined as increasing the strength of the mobile phase during a chromatographic analysis. The net effect of gradient elution is to shorten the retention time of compounds strongly retained on the analytical column. Gradient elution may be stepwise on continuous.

5.5 Method detection limit (MDL) - the minimum concentration of a substance that can be measured and reported with confidence and that the value is above zero.

5.6 Kuderna-Danish apparatus - the Kuderna-Danish (KD) appartus is a system for concentrating materials dissolved in volatile solvents.

5.7 Reverse phase liquid chromatography - reverse phase liquid chromatography involves a non-polar absorbent (C-18,ODS) coupled with a polar solvent to separate non-polar compounds.

5.8 Guard column - guard columns in HPLC are usually short (5cm) columns attached after the injection port and before the analytial column to prevent particles and strongly retained compounds from accumulating on the analytical column. The guard column should always be the same stationary phase as the analytical column and is used to extend the life of the analytical column.

5.9 MS-SIM - the GC is coupled to a select ion mode (SIM) detector where the instrument is programmed to acquire data for only the target compounds and to disregard all others. This is performed using SIM coupled to retention time discriminators. The SIM analysis procedure provides quantitative results.

5.10 Sublimation - Sublimation is the direct passage of a substance from the solid state to the gaseous state and back into the solid form without at any time appearing in the liquid state. Also applied to the conversion of solid to vapor without the later return to solid state, and to a conversion directly from the vapor phase to the solid state.

5.11 Surrogate standard - A surrogate standard is a chemically inert compound (not expected to occur in the environmental sample) which is added to each sample, blank and matrix spiked sample before extraction and analysis. The recovery of the surrogate standard is used to monitor unusual matrix effects, gross sample processing errors, etc. Surrogate recovery is evaluated for acceptance by determining whether the measured concentration falls within acceptable limits.

5.12 Retention time window - Retention time window is determined for each analyte of interest and is the time from injection to elution of a specific chemical from a chromatographic column. The window is determined by three injections of a single component standard over a 72-hr period as plus or minus three times the standard deviation of the absolute retention time for that analyte.

6. Interferences

6.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that result in discrete artifacts and/or elevated baselines in the detector profiles. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks.

6.1.1 Glassware must be scrupulously cleaned (33). Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. This should be followed by detergent washing with hot water, and rinsing with tap water and reagent water. It should then be drained dry, solvent rinsed with acetone and spectrographic grade hexane. After drying and rinsing, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Glassware should be stored inverted or capped with aluminum foil.

6.1.2 The use of high purity water, reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

6.1.3 Matrix interferences may be caused by contaminants that are coextracted from the sample. Additional clean-up by column chromatography may be required (see Section 12.4).

6.2 The extent of interferences that may be encountered using liquid chromatographic techniques has not been fully assessed. Although GC and HPLC conditions described allow for unique resolution of the specific PAH compounds covered by this method, other PAH compounds may interfere. The use of column chromatography for sample clean-up prior to GC or HPLC analysis will eliminate most of these interferences. The analytical system must, however, be routinely demonstrated to be free of internal contaminants such as contaminated solvents, glassware, or other reagents which may lead to method interferences. A laboratory reagent blank is run for each batch of reagents used to determine if reagents are contaminant-free.

6.3 Although HPLC separations have been improved by recent advances in column technology and instrumentation, problems may occur with baseline noise, baseline drift, peak resolution and changes in sensitivity. Problems affecting overall system performance can arise (34). The user is encouraged to develop a standard operating procedure (SOP) manual specific for his laboratory to minimize problems affecting overall system performance.

6.4 Concern during sample transport and analysis is mentioned. Heat, ozone, NO_2 and ultraviolet (UV) light may cause sample degradation. These problems should be addressed as part of the user prepared standard operating procedure manual. Where possible, incandescent or UV-shield fluorescent lighting should be used during analysis.

7. Safety

7.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified for the analyst (35-37).

7.2 Benzo[a]pyrene has been tentatively classified as a known or suspected, human or mammalian carcinogen. Many of the other PAHs have been classified as carcinogens. Care must be exercised when working with these substances. This method does not purport to address all of the safety problems associated with its use. It is the responsibility of whoever uses this method to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. The user should be thoroughly familiar with the chemical and physical properties of targeted substances (Table 1.0 and Figure 1.0).

7.3 Treat all selective polynuclear aromatic hydrocarbons as carcinogens. Neat compounds should be weighed in a glove box. Spent samples and unused standards are toxic waste and should be disposed according to regulations. Regularly check counter tops and equipment with "black light" for fluorescence as an indicator of contamination.

7.4 Because the sampling configuration (filter and backup adsorbent) has demonstrated greater than 95% collection efficiency for targeted PAHs, no field recovery evaluation will occur as part of this procedure.

8. Apparatus

8.1 Sample Collection

8.1.1 General Metal Works (GMW) Model PS-1 Sampler, or equivalent [General Metal Works, Inc., 145 South Miami Ave., Village of Cleves, Ohio, 45002, (800-543-7412)].

8.1.2 At least two Model PS-1 sample cartridges and filters assembled for PS-1 sampler.

8.1.3 GMW Model PS-1 calibrator and associated equipment - General Metal Works, Inc., Model GMW-40, 145 South Miami Ave., Village of Cleves, Ohio, 45002, (800-543-7412).

8.1.4 Ice chest - to store samples at 0°C after collection.

8.1.5 Data sheets for each sample for recording the location and sample time, duration of sample, starting time, and volume of air sampled.

8.1.6 Airtight, labeled screw-capped container sample cartridges (wide mouth, preferrably glass with Teflon seal or other non-contaminating seals) to hold filter and adsorbent cartridge during transport to analytical laboratory.

8.1.7 Portable Tripod Sampler (optional) - user prepared (38).

8.2 Sample Clean-up and Concentration

8.2.1 Soxhlet extractors capable of extracting GMW Model PS-1 filter and adsorbent cartridges (2.3" x 5" length), 500 mL flask, and condenser.

8.2.2 Pyrex glass tube furnace system for activating silica gel at 180°C under purified nitrogen gas purge for an hour, with capability of raising temperature gradually.

8.2.3 Glass vial, 40 mL.

8.2.4 Erlenmeyer flask, 50 mL - best source. [Note: Reuse of glassware should be minimized to avoid the risk of cross-contamination. All glassware that is used, especially glassware that is reused, must be scrupulously cleaned as soon as possible after use. Rinse glassware with the last solvent used in it and then with high-purity acetone and hexane. Wash with hot water containing detergent. Rinse with copious amount of tap water and several portions of distilled water. Drain, dry, and heat a muffle furnace at 400°C for 2 to 4 hours. Volumetric glassware must not be heated in a muffle furnace; rather, it should be rinsed with high-purity acetone and hexane. After the glassware is dry and cool, rinse it with hexane, and store it inverted or capped with solvent-rinsed aluminum foil in a clean environment.]

8.2.5 Polyester gloves for handling cartridges and filters.

8.2.6 Minivials - 2 mL, borosilicate glass, with conical reservoir and screw caps lines with Teflon-faced silicone disks, and a vial holder.

8.2.7 Stainless steel Teflon® coated spatulas and spoons.

8.2.8 Kuderna-Danish (KD) apparatus - 500 mL evaporation flask (Kontes K-570001-500 or equivalent), 10 mL graduated concentrator tubes (Knotes K-570050-1025 or equivalent) with ground-glass stoppers, and 3-ball macro Snyder Column (Kontes K-5700010500, K-50300-0121, and K-569001-219, or equivalent).

8.2.9 Adsorption columns for column chromatography - 1-cm x 10-cm with stands.

8.2.10 Glove box for working with extremely toxic standards and reagents with explosion-proof hood for venting fumes from solvents, reagents, etc.

8.2.11 Vacuum Oven - Vacuum drying oven system capable of maintaining a vacuum at 240 torr (flushed with nitrogen) overnight.

8.2.12 Concentrator tubes and a nitrogen evaporation apparatus with variable flow rate - best source.

8.2.13 Laboratory refrigerator with chambers operating at 0°C and 4°C.

8.2.14 Boiling chips - solvent extracted, 10/40 mesh silicon carbide or equivalent.

8.2.15 Water bath - heated, with concentric ring cover, capable of temperature control (± 5°C).

8.2.16 Vortex evaporator (optional).

8.3 Sample Analysis

8.3.1 Gas Chromatography with Flame Ionization Detection (FID).

8.3.1.1 Gas chromatography: Analytical system complete with gas chromatography suitable for on-column injections and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak areas and/or peak heights is recommended.

8.3.1.2 Packed Column: 1.8-m x 2-mm I.D. glass column packed with 3% OV-17 on Chromosorb W-AW-DMCS (100/120 mesh) or equivalent (Supelco Inc., Supelco Park, Bellefonte, Pa. Supelco SPB-5).

8.3.1.3 Capillary Column: 30-m x 0.25-mm ID fused silica column coated with 0.25 u thickness 5% phenyl, 90% methyl siloxane (Supelco Inc., Supelco Park, Bellefonte, Pa.).

8.3.1.4 Detector: Flame Ionization (FI)

8.3.2 Gas Chromatograph with Mass Spectroscopy Detection Coupled with Data Processing System (GC/MS/DS).

8.3.2.1 The GC must be equipped for temperature programming, and all required accessories must be available, including syringes, gases, and a capillary column. The GC injection port must be designed for capillary columns. The use of splitless injection techniques is recommended. On-column injection techniques can be used but they may severely reduce column lifetime for nonchemically bonded columns. In this protocol, a 1-3 uL injection volume is used consistently. With some GC injection ports, however, 1 uL injections may produce some improvement in precision and chromatographic separation. A 1 uL injection volume may be used if adequate sensitivity and precision can be achieved. [NOTE: If 1 uL is used as the injection volume, the injection volumes for all extracts, blanks, calibration solutions and performance check samples must be 1 uL.]

8.3.2.2 Gas Chromatograph-Mass Spectrometer Interface. The gas chromatograph is usually coupled directly to the mass spectrometer source. The interface may include a diverter valve for shunting the column effluent and isolating the mass spectrometer source. All components of the interface should be glass or glass-lined stainless steel. The interface components should be compatible with 320°C temperatures. Cold spots and/or active surfaces (adsorption sites) in the GC/MS interface can cause peak tailing and peak broadening. It is recommended that the GC column be fitted directly into the MS source. Graphic ferrules should be avoided in the GC injection area since they may adsorb PAHs. Vespel® or equivalent ferrules are recommended.

8.3.2.3 Mass Spectrometer. The static resolution of the instrument must be maintained at a minimum of 10,000 (10 percent valley). The mass spectrometer should be operated in the selected ion mode (SIM) with a total cycle time (including voltage reset time) of one second or less (Section 14.2).

8.3.2.4 Mass spectrometer: Capable of scanning from 35 to 500 amu every 1 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets all of the criteria (Section 14.5.1).

8.3.2.5 Data System. A dedicated computer data system is employed to control the rapid multiple ion monitoring process and to acquire the data. Quantification data (peak areas or peak heights) and multi-ion detector (MID) traces (displays of intensities of each m/z being monitored as a function of time) must be acquired during the analyses. Quantifications may be reported based upon computer-generated peak areas or upon measured peak heights (chart recording). The detector zero setting must allow peak-to-peak measurement of the noise on the baseline.

8.3.2.6 GC Column. A fused silica column (50-m x 0.25-mm I.D.) HP Ultra #2 crosslinked 5% phenyl methylsilicone, 0.25 um film thickness (Hewlett-Packard Co., Crystal Lake, IL) is utilized to separate individual PAHs. Other columns may be used for determination of PAHs. Minimum acceptance criteria must be determined as per Section 14.2. At the beginning of each 12-hour period (after mass resolution has been demonstrated) during which sample extracts or concentration calibration solutions will be analyzed, column operating conditions must be attained for the required separation on the column to be used for samples.

8.3.2.7 Balance - Mettler balance or equivalent.

8.3.2.8 All required syringes, gases, and other pertinent supplies to operate the GC/MS system.

8.3.2.9 Pipettes, micropipettes, syringes, burets, etc., to make calibration and spiking solutions, dilute samples if necessary, etc., including syringes for accurately measuring volumes such as 25 uL and 100 uL.

8.3.3 High Performance Liquid Chromatography (HPLC) System.

8.3.3.1 Gradient HPLC system - Consisting of acetonitrile and water phase reservoirs; mixing chamber; a high pressure pump; an injection valve (automatic sampler with an optional 25 uL loop injector); a Vydac C-18 bonded phase reverse phase (RP) column, (The Separations Group, P.O. Box 867, Hesperia, CA 92345) or equivalent (25-cm x 4.6-mm ID); a variable wavelength UV/Fluorescence detector and a data system or strip chart recorder. A Spectra Physics 8100 liquid chromatograph multi-microprocessor controlled, with ternary gradient pumping system, constant flow, autosampler injector (10 uL injection loop), and column oven (optional).

8.3.3.2 Guard column - 5-cm guard column pack with Vydac reverse phase C-18 material.

8.3.3.3 Reverse phase analytical column - Vydac or equivalent, C-18 bonded phase RP column (The Separation Group, P.O. Box 867, Hesperia, Ca., 92345), 4.6-mm x 25-cm, 5-micron particle diameter.

8.3.3.4 LS-4 fluorescence spectrometer, Perkin Elmer, sepaate excitation and emission, monochromator positioned by separate microprocessor-controlled flow cell and wavelength programming ability (optional).

8.3.3.5 Ultraviolet/visible detector, Spectra Physics 8440, deuterium Lamp, capable of programmable wavelengths (optional).

8.3.3.6 Dual channel Spectra Physics 4200 Computing Integrator, measures peak areas and retention times from recorded chromatographs. IBM PC XT will Spectra Physics Labnet system for data collection and storage (optional).

9. Reagents and Materials

9.1 Sample Collection

9.1.1 Acid-washed quartz fiber filter - 105 mm micro quartz fiber binderless filter (General Metal Works, Inc., Cat. No. GMW QMA-4, 145 South Miami Ave., Village of Cleves, Ohio, 45002 [800-543-7412] or Supelco Inc., Cat. No. 1-62, Supelco Park, Bellefonte, PA, 16823-0048).

9.1.2 Polyurethane foam (PUF) - 3 inch thick sheet stock, polyether type (density 0.022 g/cm^3) used in furniture upholstering (General Metal Works, Inc., Cat. No. PS-1-16, 145 South Miami Ave., Village of Cleves, Ohio, 45002 [800-543-7412] or Supelco Inc., Cat. No. 1-63, Supelco Park, Bellefonte, PA, 16823-0048).

9.1.3 XAD-2 resin - Supelco Inc., Cat. No. 2-02-79, Supelco Park, Bellefonte, PA, 16823-0048.

9.1.4 Hexane-rinsed aluminum foil - best source.

9.1.5 Hexane-reagent grade, best source.

9.2 Sample Clean-up and Concentration

9.2.1 Soxhlet Extraction

9.2.1.1 Methylene chloride - chromatographic grade, glass-distilled, best source

9.2.1.2 Sodium sulfate, anhydrous - (ACS) granular anhydrous (purified by washing with methylene chloride followed by heating at 400°C for 4 hrs in a shallow tray).

9.2.1.3 Boiling chips - solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

9.2.1.4 Nitrogen - high purity grade, best source.

9.2.1.5 Ether - chromatographic grade, glass-distilled, best source.

9.2.1.6 Hexane - chromatographic grade, glass-distilled, best source.

9.2.1.7 Dibromobiphenyl - chromatographic grade, best source. Used for internal standard.

9.2.1.8 Decafluorobiphenyl - chromatographic grade, best source. Used for internal standard.

9.2.2 Solvent Exchange

9.2.2.1 Cyclohexane - chromatographic grade, glass-distilled, best source.

9.2.3 Column Clean-up

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9.2.3.1 Silica gel - high purity grade, type 60, 70-230 mesh; extracted in a Soxhlet apparatus with methylene chloride for 6 hours (minimum of 3 cycles per hour) and activated by heating in a foil-covered glass container for 24 hours at 130°C.

9.2.3.2 Sodium sulfate, anhydrous - (ACS) granular anhydrous (See Section 9.2.1.2).

9.2.3.3 Pentane - chromatographic grade. glass-distilled, best source.

Lobar Prepacked Column

9.2.3.4 Silica gel lobar prepacked column - E. Merck, Darmstadt, Germany [Size A(240-10) Lichroprep Si (40-63 um)].

9.2.3.5 Precolumn containing sodium sulfate - American Chemical Society (ACS) granular anhydrous (purified by washing with methylene chloride followed by heating at 400°C for 4 hours in a shallow tray).

9.2.3.6 Hexane - chromatographic grade, glass-distilled, best source.

9.2.3.7 Methylene chloride - chromatographic grade, glass-distilled, best source

9.2.3.8 Methanol - chromatographic grade, glass-distilled, best source.

9.3 Sample Analysis

9.3.1 Gas Chromatography Detection

9.3.1.1 Gas cylinders of hydrogen and helium - ultra high purity, best source.

9.3.1.2 Combustion air - ultra high purity, best source.

9.3.1.3 Zero air - Zero air may be obtained from a cylinder or zero-grade compressed air scrubbed with Drierite® or silica gel and 5A molecular sieve or activated charcoal, or by catalytic cleanup of ambient air. All zero air should be passed through a liquid argon cold trap for final cleanup.

9.3.1.4 Chromatographic-grade stainless steel tubing and stainless steel plumbing fittings - for interconnections. [Alltech Applied Science, 2051 Waukegan Road, Deerfield, IL, 60015, (312) 948-8600]. [Note: All such materials in contact with the sample, analyte, or support gases prior to analysis should be stainless steel or other inert metal. Do not use plastic or Teflon® tubing or fittings.]

9.3.1.5 Native and isotopically labeled PAHs isomers for calibration and spiking standards-[Cambridge Isotopes, 20 Commerce Way, Woburn, MA, 01801 (617-547-1818)]. Suggested isotopically labeled PAH isomers are:

- perylene - d_{12}
- chrysene - d_{12}
- acenaphthene - d_{10}
- naphthalene - d_8
- phenanthrene - d_{10}

9.3.1.6 Decafluorotriphenylphosphine (DFTPP) - best source, used for tuning GC/MS.

9.3.2 High Performance Liquid Chromatography Detection

9.3.2.1 Acetonitrile - chromatographic grade, glass-distilled, best source.

9.3.2.2 Boiling chips - solvent extracted, approximatley 10/40 mesh (silicon carbide or equivalent).

9.3.2.3 Water - HPLC Grade. Water must not have an interference that is observed at the minimum detectable limit (MDL) of each parameter of interest.

9.3.2.4 Decafluorobiphenyl - HPLC grade, best source (used for internal standard).

10. Preparation of Sample Filter and Adsorbent

10.1 Sampling Head Configuration

10.1.1 The sampling head (Figure 2) consist of a filter holder compartment followed by a glass cartridge for retaining the adsorbent.

10.1.2 Before field use, both the filter and adsorbent must be cleaned to <10 ng/apparatus of B[a]P or other PAHs.

10.2 Glass Fiber Filter Preparation

10.2.1 The glass fiber filters are baked at 600°C for five hours before use. To insure acceptable filters, they are extracted with methylene chloride in a Soxhlet apparatus, similar to the cleaning of the XAD-2 resin (see Section 10.3).

10.2.2 The extract is concentrated and analyzed by either GC or HPLC. A filter blank of <10 ng/filter of B[a]P or other PAHs is considered acceptable for field use.

10.3 XAD-2 Adsorbent Preparation

10.3.1 For initial cleanup of the XAD-2, a batch of XAD-2 (approximately 60 grams) is placed in a Soxhlet apparatus [see Figure 3(a)] and extracted with methylene chloride for 16 hours at approximately 4 cycles per hour.

10.3.2 At the end of the initial Soxhlet extraction, the spent methylene chloride is discarded and replaced with fresh reagent. The XAD-2 resin is once again extracted for 16 hours at approximately 4 cycles per hour.

10.3.3 The XAD-2 resin is removed from the Soxhlet apparatus, places in a vacuum oven connected to an ultra-purge nitrogen gas stream and dries at room temperature for approximately 2-4 hours (until no solvent odor is detected).

10.3.4 A nickel screen (mesh size 200/200) is fitted to the bottom of a hexane-rinsed glass cartridge to retain the XAD-2 resin.

10.3.5 The Soxhlet extracted/vacuum dried XAD-2 resin is placed into the sampling cartridge (using polyester gloves) to a depth of approximately 2 inches. This should require approximately 55 grams of adsorbent.

10.3.6 The glass module containing the XAD-2 adsorbent is wrapped with hexane-rinsed aluminum foil, placed in a labeled container and tightly sealed with Teflon® tape.

10.3.7 At least one assemble cartridge from each batch must be analyzed, as a laboratory blank, using the procedures described in Section 13, before the batch is considered acceptable for field use. A blank of <10 ng/cartridge of B[a]P on other PNA's is considered acceptable.

10.4 PUF Sampling Cartridge Preparation

10.4.1 The PUF adsorbent is a polyether-type polyurethane foam (density No. 3014 or 0.0225 g/cm^3) used for furniture upholstery.

10.4.2 The PUF inserts are 6.0-cm diameter cylindrical plugs cut from 3-inch sheet stock and should fit, with slight compression, in the glass cartridge, supported by the wire screen (see Figure 1). During cutting, the die is rotated at high speed (e.g., in a drill press) and continuously lubricated with water.

10.4.3 For initial cleanup, the PUF plug is placed in a Soxhlet apparatus [see Figure 3(a)] and extracted with acetone for 14-24 hours at approximately 4 cycles per hour. [Note: When cartridges are reused, 5% diethyl ether in n-hexane can be used as the cleanup solvent.]

10.4.4 The extracted PUF is placed in a vacuum oven connected to a water aspirator and dried at room temperature for approximately 2-4 hours (until no solvent odor is detected).

10.4.5 The PUF is placed into the glass sampling cartridge using polyester gloves. The module is wrapped with hexane-rinsed aluminum foil, placed in a labeled container, and tightly sealed.

10.4.6 At least one assembled cartridge from each batch must be analyzed, as a laboratory blank, using the procedures described in Section 13, before the batch is considered acceptable for field use. A blank level of <10 ng/plug for single compounds is considered to be acceptable.

11. Sample Collection

11.1 Description of Sampling Apparatus

11.1.1 The entire sampling system can be a modification of a traditional high volume sampler (see Figure 4) or a portable sampler (see Figure 5). A unit specifically designed for this method is commercially available (Model PS-1 - General Metal Works, Inc., Village of Cleves, Ohio).

11.1.2 The sampling module consists of a glass sampling cartridge and an air-tight metal cartridge holder, as outlined in Section 10.1. The adsorbent (XAD-2 or PUF) is retained in the glass sampling cartridge.

11.2 Calibration of Sampling System

Each sampler is to be calibrated: 1) when new; 2) after major repairs or maintenance; 3) whenever any audit point deviates from the calibration curve by more than 7%; 4) when a different sample collection media, other than that which the sampler was originally calibrated to, will be used for sampling; or 5) at the frequency specified in the user Standard Operating Procedure (SOP) manual in which the samplers are utilized.

11.2.1 Calibration of Flow Rate Transfer Standard

Calibration of the modified high volume air sampler in the field is performed using a calibrated orifice flow rate transfer standard. The flow rate transfer standard must be certified in the laboratory against a positive displacement rootsmeter (see Figure 6). Once certified, the recertification is performed rather infrequently if the orifice is protected from damage. Recertification of the orifice flow rate transfer standard is performed once per year utilizing a set of five (5) multihole resistance plates. [Note: The 5 multihole resistance plates are used to change the flow through the orifice so that several points can be obtained for the orifice calibration curve.]

11.2.1.1 Record the room temperature (t_1 in °C) and barometric pressure (P_b in mm Hg) on Orifice Calibration Data Sheet (see Figure 7). Calculate the room temperature in °K (absolute temperature) and record on Orifice Calibration Data Sheet.

$$t_1 \text{ in K} = 273° + t_1 \text{ in °C}$$

11.2.1.2 Set up laboratory orifice calibration equipment as illustrated in Figure 6. Check the oil level of the rootsmeter prior to starting. There are three oil level indicators, one at the clear plastic end, and two sight glasses, one at each end of the measuring chamber.

11.2.1.3 Check for leaks by clamping both manometer lines blocking the orifice with cellophane tape, turning on the high volume motor, and noting any change in the rootsmeter's reading. If the rootsmeter's reading changes, then there is a leak in the system or in the tape. Eliminate the leak before proceeding. If the rootsmeter's reading remains constant, turn off the hi-vol motor, remove the cellophane tape, and unclamp both manometer lines.

11.2.1.4 Install the 5-hole resistance plate between the orifice and the filter adapter.

11.2.1.5 Turn manometer tubing connectors one turn counterclockwise. Make sure all connectors are open.

11.2.1.6 Adjust both manometer midpoints by sliding their movable scales until the zero point corresponds with the bottom of the meniscus. Gently shake or tap to remove any air bubbles and/or liquid remaining on tubing connectors. (If additional liquid is required for the water manometer, remove tubing connector and add clean water).

11.2.1.7 Turn on the hi-vol motor and let it run for five minutes to set the motor brushes.

11.2.1.8 Record both manometer readings-orifice water manometer (ΔH) and rootsmeter mercury manometer (ΔP). [Note: ΔH is the sum of the difference from zero (0) of the two column heights.]

11.2.1.9 Record the time, in minutes, required to pass a known volume of air (approximately 200-300 ft^3 of air for each resistance plate) through the rootsmeter by using the rootsmeter's digital volume dial and a stopwatch.

11.2.1.10 Turn off the high volume motor.

11.2.1.11 Replace the 5-hole resistance plate with the 7-hole resistance plate.

11.2.1.12 Repeat Sections 11.2.1.3 through 11.2.1.10.

11.2.1.13 Repeat for each resistance plate. Note results on Orifice Calibration Data Sheet (see Figure 7). Only a minute is needed for warm-up of the motor. Be sure to tighten the orifice enough to eliminate any leaks. Also check the gaskets for cracks. [Note: The placement of the orifice prior to the rootsmeter causes the pressure at the inlet of the rootsmeter to be reduced below atmospheric conditions, thus causing the measured volume to be incorrect. The volume measured by the rootsmeter must be corrected.]

11.2.1.14 Correct the measured volumes with the following formula and record the standard volume on the Orifice Calibration Data Sheet:

$$V_{std} = V_m \frac{P_1 - \Delta P}{P_{std}} \frac{T_{std}}{T_1}$$

where: V_{std} = standard volume (std m^3).

V_m = actual volume measured by the rootsmeter (m^3).

P_1 = barometric pressure during calibration (mm Hg).

ΔP = differential pressure at inlet to volume meter (mm Hg).

P_{std} = 760 mm Hg.

T_{std} = 298 K.

T_1 = ambient temperature during calibration (K).

11.2.1.15 Record standard volume on Orifice Calibration Data Sheet.

11.2.1.16 The standard flow rate as measured by the rootsmeter can now be calculated using the following formula:

$$Q_{std} = \frac{V_{std}}{\theta}$$

where: Q_{std} = standard volumetric flow rate, std m3/min.

θ = elapsed time, min.

11.2.1.17 Record the standard flow rates to the nearest 0.01 std m^3/min.

11.2.1.18 Calculate and record $\sqrt{\Delta H(P_1/P_{std})(298/T_1)}$ value for each standard flow rate.

11.2.1.19 Plot each $\sqrt{\Delta H(P_1/P_{std})(298/T_1)}$ value (y-axis) versus its associated standard flow rate (x-axis) on arithmetic graph paper, draw a line of best fit between the individual plotted points and calculate the linear regression slope (M) and intercept (b).

11.2.1.20 Commercially available calibrator kits are available [General Metal Works Inc., Model GMW-40, 145 South Miami Avenue, Village of Cleves, Ohio, 45002 (1-800-543-7412)].

11.2.2 Calibration of The High Volume Sampling System Utilizing Calibrated Multi-point Flow Rate Transfer Standard

11.2.2.1 The airflow through the sampling system can be monitored by a venturi/magnehelic assembly, as illustrated in Figure 4 or by a u-tube assembly connected to the high volume portable design as illustrated in Figure 5. The field sampling system must be audited every six months using a flow rate transfer standard, as described in the U.S. EPA High Volume Sampling Method, 40 CFR 50, Appendix B. A single-point calibration must be performed before and after each sample collection, using a transfer standard calibrated as described in Section 11.2.1.

11.2.2.2 Prior to initial multi-point calibration, a "dummy" adsorbent cartridge and filter are placed in the sampling head and the sampling motor is activated. The flow control valve is fully opened and the voltage variator is adjusted so that a sample flow rate corresponding to 110% of the desired flow rate (typically 0.20 - 0.28 m^3/min) is indicated on the Magnehelic gauge (based on the previously obtained multi-point calibration curve). The motor is allowed to warm up for 10 minutes and then the flow control valve is adjusted to achieve the desired flow rate. Turn off the sampler. The ambient temperature and barometric pressure should be recorded on the Field Calibration Data Sheet (Figure 9).

11.2.2.3 The flow rate transfer standard is placed on the sampling head, and a manometer is connected to the tap on the transfer standard using a length of tubing. Properly align the retaining rings with filter holder and secure by tightening the three screw clamps. Set the zero level of the manometer. Attach the magnehelic gage to the sampler venturi quick release connections. Adjust the zero (if needed) using the zero adjust screw on the face of the gage.

11.2.2.4 Turn the flow control valve to the fully open position and turn the sampler on. Adjust the flow control valve until a magnehelic reading of approximately 70 in. is obtained. Allow the magnehelic and manometer readings to stabilize and record these values.

11.2.2.5 Adjust the flow control valve and repeat until six or seven uniformally spaced magnehelic readings are recorded spanning the range of approximately 40-70 in. Record the readings on the Field Calibration Data Sheet (see Figure 9). [Note: Use of some filter/sorbent media combinations may restrict the airflow resulting in a maximum magnehelic reading of 60 in. or less. In such cases, a variable transformer should be placed in-line between the 110 volt power source and the sampler so that the line voltage can be increased sufficiently to obtain a maximum magnehelic reading approaching 70 in.].

11.2.2.6 Adjust the orifice manometer reading for standard temperature and pressure using the following equation:

$$X = \sqrt{\Delta H \frac{P_a}{P_{std}} \quad \frac{T_{std}}{T_a}}$$

where: X = adjusted manometer reading to standard temperature and pressure (in. water).

ΔH = observed manometer reading (in water).

P_a = current barometric pressure (mm Hg).

P_{std} = 760 mm Hg.

T_a = current temperature (K), (K = °C + 273).

T_{std} = standard temperature (298 K).

11.2.2.7 Calculate the standard flow rate for each corrected manometer reading by the following equation:

$$Q_{std} = \frac{X - b}{M}$$

where:

Q_{std} = standard flow rate (m^3/min).

M = slope of flow rate transfer standard calibration curve.

X = corrected manometer reading from 11.2.2.6 (in water).

b = intercept of flow rate transfer standard calibration curve.

11.2.2.8 Adjust the magnehelic gage readings to standard temperature and pressure using the following equation:

$$M_{std} = \sqrt{\frac{(M)(P_a)}{P_{std}} \quad \frac{T_{std}}{T_a}}$$

where:

M_{std} = adjusted magnehelic reading to standard temperature and pressure (inches of water).

M = observed magnehelic reading (inches of water).

P_a = ambient atmospheric pressure (mm Hg).

P_{std} = standard pressure (760 mm Hg).

T_a = ambient temperature (K), (K = °C + 273).

T_{std} = standard temperature (298 K).

11.2.2.9 Plot each M_{std} value (y-axis) versus its associated Q_{std} standard (x-axis) on arithmetic graph paper. Draw a line of best fit between the individual plotted points. This is the calibration curve for the venturi. Retain with sampler.

11.2.2.10 Record the corresponding Q_{std} for each M_{std} under Q_{std} column on Field Calibration Data Sheet, Figure 9.

11.2.3 Single-point Audit of The High Volume Sampling System Utilizing Calibrated Flow Rate Transfer Standard

11.2.3.1 A single point flow audit check is performed before and after each sampling period utilizing the Calibration Flow Rate Transfer Standard (Section 11.2.1).

11.2.3.2 Prior to single point audit, a "dummy" adsorbent cartridge and filter are placed in the sampling head and the sampling motor is activated. The flow control valve is fully opened and the voltage variator is adjusted so that a sample flow rate corresponding to 110% of the desired flow rate (typically 0.20-0.28 m^3/min) is indicated on the magnehelic gauge (based on the previously obtained multi-point calibration curve). The motor is allowed to warm up for 5 minutes and then the flow control valve is adjusted to achieve the desired flow rate. Turn off the sampler. The ambient temperature and barometric pressure should be recorded on a Field Test Data Sheet (Figure 10).

11.2.3.3 The flow rate transfer standard is placed on the sampling head.

11.2.3.4 Properly align the retaining rings with filter holder and secure by tightening the three screw clamps.

11.2.3.5 Using tubing, attach one manometer connector to the pressure tap of the transfer standard. Leave the other connector open to the atmosphere.

11.2.3.6 Adjust the manometer midpoint by sliding the movable scale until the zero point corresponds with the water meniscus. Gently shake or tap to remove any air bubbles and/or liquid remaining on tubing connectors. (If additional liquid is required, remove tubing connector and add clean water.)

11.2.3.7 Turn on high volume motor and let run for five minutes.

11.2.3.8 Record the pressure differential indicated, ΔH, in inches of water. Be sure stable ΔH has been established.

11.2.3.9 Record the observed magnehelic gauge reading, in inches of water. Be sure stable M has been established.

11.2.3.10 Using previously established Flow Rate Transfer Standard curve, calculate Q_{std} (see steps 11.2.2.6 - 11.2.2.7).

11.2.3.11 Using previously established venturi calibration curve, calculate the indicated Q_{std} (Section 11.2.2.9).

11.2.3.12 A multi-point calibration of the Flow Rate Transfer Standard against a primary standard, must be obtained annually, as outlined in Section 11.2.1.

11.2.3.13 Remove Flow Rate Transfer Standard and dummy adsorbent cartridge and filter assembly.

11.3 Sample Collection

11.3.1 After the sampling system has been assembled and flow checked as described in Sections 11.1 and 11.2, it can be used to collect air samples, as described in Section 11.3.2.

11.3.2 The samples should be located in an unobstructed area, at least two meters from any obstacle to air flow. The exhaust hose should be stretched out in the downwind direction to prevent recycling of air into the sample head.

11.3.3 With the empty sample module removed from the sampler, rinse all sample contact areas using reagent grade hexane in a Teflon® squeeze bottle. Allow the hexane to evaporate from the module before loading the samples.

11.3.4 Detach the lower chamber of the rinsed sampling module. While wearing disposable clean lint-free nylon or powder-free surgical gloves, remove a clean glass cartridge/sorbent from its container (wide mouthed glass jar with a Teflon®-lined lid) and unwrap its aluminum foil covering. The foil should be replaced back in the sample container to be reused after the sample has been collected.

11.3.5 Insert the cartridge into the lower chamber and tightly reattach it to the module.

11.3.6 Using clean Teflon® tipped forceps, carefully place a clean fiber filter atop the filter holder and secure in place by clamping the filter holder ring over the filter using the three screw clamps. Insure that all module connections are tightly assembled. [Note: Failure to do so could result in air flow leaks at poorly sealed locations which could affect sample representativeness]. Ideally, sample module loading and unloading should be conducted in a controlled environment or at least a centralized sample processing area so that the sample handling variables can be minimized.

11.3.7 With the module removed from the sampler and the flow control valve fully open, turn the pump on and allow it to warm-up for approximately 5 minutes.

11.3.8 Attach a "dummy" sampling module loaded with the exact same type of filter and sorbent media as that which will be used for sample collection.

11.3.9 With the sampler off, attach the Magnahelic gage to the sampler. Turn the sampler on and adjust the flow control valve to the desired flow (normally as indicated by the cfm) magnahelic gauge reading and reference by the calibration chart. [Note: Breakthrough has not been a problem for all PAHs outlined in Section 1.5 using this sampling method except anthracene and penanthrene]. Once the flow is properly adjusted, extreme care should be taken not to inadvertantly alter its setting.

11.3.10 Turn the smpler off and remove both the "dummy" module and the Magnahelic gauge. The sampler is now ready for field use.

11.3.11 The zero reading of the sampler Magnehelic is checked. Ambient temperature, barometric pressure, elapsed time meter setting, sampler serial number, filter number, and adsorbent sample number are recorded on the Field Test Data Sheet (see Figure 10). Attach the loaded sampler module to the sampler.

11.3.12 The voltage variator and flow control valve are placed at the settings used in Section 11.2.2, and the power switch is turned on. The elapsed time meter is activated and the start time is recorded. The flow (Magnehelic setting) is adjusted, if necessary, using the flow control valve.

11.3.13 The Magnehelic reading is recorded every six hours during the sampling period. The calibration curve

(Section 11.2.4) is used to calculate the flow rate. Ambient temperature, barometric pressure, and Magnehelic reading are recorded at the beginning and end of the sampling period.

11.3.14 At the end of the desired sampling period, the power is turned off. Carefully remove the sampling head containing the filter and adsorbent cartridge to a clean area.

11.3.15 While wearing disposable lint free nylon or surgical gloves, remove the sorbent cartridge from the lower module chamber and lay it on the retained aluminum foil in which the sample was originally wrapped.

11.3.16 Carefully remove the glass fiber filter from the upper chamber using clean Teflon® tiped forceps.

11.3.17 Fold the filter in half twice (sample side inward) and place it in the glass cartridge atop the sorbent.

11.3.18 Wrap the combined samples in aluminum foil and place them in their original glass sample container. A sample label should be completed and affixed to the sample container. Chain-of-custody should be maintained for all samples.

11.3.19 The glass containers should be stored in ice and protected from light to prevent possible photo-decomposition of collected analytes. If the time span between sample collection and laboratory analysis is to exceed 24 hours, sample must be kept refrigerated. [Note: Recent studies (13,16) have indicated that PUF does not retain, during storage, B[a]P as effectively as XAD-2. Therefore, sample holding time should not exceed 20 days.]

11.3.20 A final calculated sample flow check is performed using the calibration orifice, as described in Section 11.2.2. If calibration deviates by more than 10% from the initial reading, the flow data for that sample must be marked as suspect and the sampler should be inspected and/or removed from service.

11.3.21 At least one field filter/adsorbent blank will be returned to the laboratory with each group of samples. A field blank is treated exactly as a sample except that no air is drawn through the filter/adsorbent cartridge assembly.

11.3.22 Samples are stored at 0°C in an ice chest until receipt at the analytical laboratory, after which they are refrigerated at 4°C.

12. Sample Clean-up and Concentration

[Note: The following sample extraction, concentration, solvent exchange and analysis procedures are outlined for user convenience in Figure 11.]

12.1 Sample Identification

12.1.1 The samples are returned in the ice chest to the laboratory in the glass sample container containing the filter and adsorbent.

12.1.2 The samples are logged in the laboratory logbook according to sample location, filter and adsorbent cartridge number identification and total air volume sampled (uncorrected).

12.1.3 If the time span between sample registration and analysis is greater than 24-hrs., then the samples must be kept refrigerated. Minimize exposure of samples to fluorescence light. All samples should be extracted within one week after sampling.

12.2 Soxhlet Extraction and Concentration

12.2.1 Assemble the Soxhlet apparatus [see Figure 3(a)]. Immediately before use, charge the Soxhlet apparatus with 200 to 250 mL of methylene chloride and reflux for 2 hours. Let the apparatus cool, disassemble it, transfer the methylene chloride to a clean glass container, and retain it as a blank for later analysis, if required. Place the adsorbent and filter together in the Soxhlet apparatus (the use of an extraction thimble is optional) [illegible] using XAD-2 adsorbent in the sampling module. [Note: The filter and adsorbent are analyzed together in order to reach detection limits, avoid questionable interpretation of the data, and minimize cost.] Since methylene chloride is not a suitable solvent for PUF, 10% ether in hexane is employed to extract the PAHs from the PUF resin bed separate from the methylene chloride extraction of the accompanying filter rather than methylene chloride for the extraction of the XAD-2 cartridge.

12.2.1.1 Prior to extraction, add a surrogate standard to the Soxhlet solvent. A surrogate standard (i.e., a chemically inert compound not expected to occur in an environmental sample) should be added to each sample, blank, and matrix spike sample just prior to extraction or processing. The recovery of the surrogate standard is used to monitor for unusual matrix effects, gross sample processing errors, etc. Surrogate recovery is evaluated for acceptance by determining whether the measured concentration falls within the acceptance limits. The following surrogate standards have been successfully utilized in determining matrix effects, sample process errors, etc. utilizing GC/FID, GC/MS or HPLC analysis.

Surrogate Standard	Concentration	Analytical Technique
Dibromobiphenyl	50 ng/uL	GC/FID
Dibromobiphenyl	50 ng/uL	GC/MS
Deuterated Standards	50 ng/uL	GC/MS
Decafluorobiphenyl	50 ng/uL	HPLC

[Note: The deuterated standards will be added in Section 14.3.2. Deuterated analogs of selective PAHs cannot be used as surrogates for HPLC analysis due to coelution problems.] Add the surrogate standard to the Soxhlet solvent.

12.2.1.2 For the XAD-2 and filter extracted together, add 300 mL of methylene chlorine to the apparatus and reflux for 18 hours at a rate of at least 3 cycles per hour.

12.2.1.3 For the PUF extraction separate from the filter, add 300 mL of 10 percent ether in hexane to the apparatus and reflux for 18 hours at a rate of at least 3 cycles per hour.

12.2.1.4 For the filter extraction, add 300 mL of methylene chloride to the apparatus and reflux for 18 hours at a rate of at least 3 cycles per hour.

12.2.2 Dry the extract from the Soxhlet extraction by passing it through a drying column containing about 10 grams of anhydrous sodium sulfate. Collect the dried extract in a Kuderna-Danish (K-D) concentrator assembly. Wash the extractor flask and sodium sulfate column with 100 - 125 mL of methylene chloride to complete the quantitative transfer.

12.2.3 Assemble a Kuderna-Danish concentrator [see Figure 3(b)] by attaching a 10 mL concentrator tube to a 500 mL evaporative flask. [Note: Other concentration devices (vortex evaporator) or techniques may be used in place of the K-D as long as qualitative and quantitative recovery can be demonstrated.]

12.2.4 Add two boiling chips, attach a three-ball macro-Snyder column to the K-D flask, and concentrate the extract using a water bath at 60 to 65°C. Place the K-D apparatus in the water bath so that the concentrator tube is about half immersed in the water and the entire rounded surface of the flask is bathed with water vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in one hour. At the proper rate of distillation, the balls of the column actively chatter but the chambers do not flood. When the liquid has reached an approximate volume of 5 mL, remove the K-D apparatus from the water bath and allow the solvent to drain for at least 5 minutes while cooling.

12.2.5 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 5 mL of cyclohexane.

12.3 Solvent Exchange

12.3.1 Replace the K-D apparatus equipped with a Snyder column back on the water bath.

12.3.2 Increase the temperature of the hot water bath to 95-100°C. Momentarily, remove the Snyder column, add a new boiling chip, and attach a two-ball micro-Snyder column. Prewet the Snyder column, using 1 mL of cyclohexane. Place the K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration in 15-20 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes.

12.3.3 When the apparatus is cool, remove the micro-Snyder column and rinse its lower joint into the concentrator tube with about 0.2 mL of cyclohexane. [Note: A 5 mL syringe is recommended for this operation]. Adjust the extract volume to exactly 1.0 mL with cyclohexane. Stopper the concentrator tube and store refrigerated at 4°C, if further processing will not be performed immediately. If the extract will be stored longer than 24 hours, it should be transferred to a Teflon®-sealed screw-cap vial.

12.4 Sample Cleanup By Solid Phase Exchange

Cleanup procedures may not be needed for relatively clean matrix samples. If the extract in Section 12.3.3 is clear, cleanup may not be necessary. If cleanup is not necessary, the cyclohexane extract (1 mL) can be analyzed directly by GC/FI detection, except the initial oven temperature begins at 30°C rather than 80°C for cleanup samples (see Section 13.3), or solvent exchange to acetonitrile for HPLC analysis. If cleanup is required, the procedures are presented using either handpack silica gel column as prescribed in Method 610 (see Section 18.0, citation No. 18 and 22) or the use of a Lobar prepacked silica gel column for PAH concentration and separation. Either approach can be employed by the user.

12.4.1 Method 610 Cleanup Procedure [see Figure 3(c)]

12.4.1.1 Pack a 6-inch disposable Pasture pipette (10 mm I.D. x 7 cm length) with a piece of glass wool. Push the wool to the neck of the disposable pipette. Add 10 grams of activated silica gel in methylene chloride slurry to the disposable pipette. Gently tap the column to settle the silica gel and elute the methylene chloride. Add 1 gram of anhydrous sodium sulfate to the top of the silica gel column.

12.4.1.2 Prior to initial use, rinse the column with methylene chloride at 1 mL/min for 1 hr to remove any trace of contaminants. Preelute the column with 40 mL of pentane. Discard the eluate and just prior to exposure of the sodium sulfate layer to the air, transfer the 1 mL of the cyclohexane sample extract onto the column, using an additional 2 mL of cyclohexane to complete the transfer. Allow to elute through the column.

12.4.1.3 Just prior to exposure of the sodium sulfate layer to the air, add 25 mL of pentane and continue elution of the column. Discard the pentane eluate. [Note: The pentane fraction contains the aliphatic hydrocarbons collected on the filter/ adsorbent combination. If interested, this fraction may be analyzed for specific aliphatic organics.] Elute the column with 25 mL of methylene chloride/pentane (4 + 6) (V/V) and collect the eluate in a 500 mL K-D flask equipped with a 10 mL concentrator tube. [Note: This fraction contains the B[a]P and other moderately polar PAHs]. Elution of the column should be at a rate of about 2 mL/min. Concentrate the collected fraction to less than 10 mL by the K-D technique, as illustrated in Section 12.3 using pentane to rinse the walls of the glassware. The extract is now ready for HPLC or GC analysis. [Note: An additional elution through the column with 25 mL of methanol will collect highly polar oxygenated PAHs with more than one functional group. This fraction may be analyzed for specific polar PAHs. However, additional cleanup by solid phase extraction may be required to obtain both qualitative and quantitative data due to complexity of the eluant.]

12.4.2 Lobar Prepacked Column Procedure

12.4.2.1 The setup using the Lobar prepacked column consists of an injection port, septum, pump, precolumn containing sodium sulfate, Lobar prepacked column and solvent reservoir.

12.4.2.2 The column is cleaned and activated according to the following cleanup sequence:

Fraction	Solvent Composition	Volume (mL)
1	100% Hexane	20
2	80% Hexane/20% Methylene Chloride	10
3	50% Hexane/50% Methylene Chloride	10
4	100% Methylene Chloride	10
5	95% Methylene Chloride/5% Methanol	10
6	80% Methylene Chloride/20% Methanol	10

12.4.2.3 Reverse the sequence at the end of the run and run to the 100% hexane fraction in order to activate the column. Discard all fractions.

12.4.2.4 Pre-elute the column with 40 mL of hexane, which is also discharged.

12.4.2.5 Inject 1 mL of the cyclohexane sample extract, followed by 1 mL injection of blank cyclohexane.

12.4.2.6 Continue elution of the column with 20 mL of hexane, which is also discharged.

12.4.2.7 Now elute the column with 180 mL of a 40/60 mixture of methylene chloride/hexane respectively.

12.4.2.8 Collect approximately 180 mL of the 40/60 methylene chloride/hexane mixture in a K-D concentrator assembly.

12.4.2.9 Concentrate to less than 10 mL with the K-D assembly as discussed in Section 12.2.

12.4.2.10 The extract is now ready for either HPLC or GC analysis.

13. Gas Chromatography Analysis with Flame Ionization Detection

13.1 Gas chromatography (GC) is a quantitative analytical technique useful for PAH identification. This method provides the user the flexibility of column selection (packed or capillary) and detector [flame ionization (FI) or mass spectrometer (MS)] selection. The mass spectrometer provides for specific identification of B(a)P; however, with system optimization, other PAHs may be qualitatively and quantitatively detected using MS (see Section 14.0). This procedure provides for common GC separation of the PAHs with subsequent detection by either FI or MS (see Figure 12.0). The following PAHs have been quantified by GC separation with either FI or MS detection:

Acenaphthene
Acenaphthylene
Anthracene
Benzo(a)anthracene
Benzo(a)pyrene
Benzo(b)fluoranthene
Benzo(e)pyrene
Benzo(g,h,i)perylene
Benzo(k)fluoranthene
Chrysene
Dibenzo(a,h)anthracene
Fluoranthene
Fluorene
Indeno(1,2,3-cd)pyrene
Naphthalene
Phenanthrene
Pyrene

The packed column gas chromatographic method described here can not adequately resolve the following four pairs of compounds: anthracene and phenanthrene; chrysene and benzo(a)anthracene; benzo(b)fluoranthene and benzo(k)fluoranthene; and dibenzo(a,h) anthracene and indeno(1,2,3-cd)pyrene. The use of a capillary column instead of the packed column, also described in this method, should adequately resolve these PAHs. However, unless the purpose of the analysis can be served by reporting a quantitative sum for an unresolved PAH pair, either capillary gas chromatography/mass spectroscopy (Section 14.0) or high performance liquid chromatography (Section 15.0) should be used for these compounds. This section will address the use of GC/FI detection using packed or capillary columns.

13.2 To achieve maximum sensitivity with the GC/FI method, the extract must be concentrated to 1.0 mL, if not already concentrated to 1 mL. If not already concentrated to 1 mL, add a clean boiling chip to the methylene chloride extract in the concentrator tube. Attach a two-ball micro-Snyder column. Prewet the micro-Snyder column by adding about 2.0 mL of methylene chloride to the top. Place the micro K-D apparatus on a hot water bath (60 to 65°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 minutes. At the proper rate of distillation the balls will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus. Drain and cool for at least 10 minutes. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with a small volume of methylene chloride. Adjust the final volume to 1.0 mL and stopper the concentrator tube.

13.3 Assemble and establish the following operating parameters for the GC equipped with an FI detector:

	Capillary		Packed
	(A)	(B)	
Identification	SPB-5 fused silica capillary, 0.25 um 5% phenyl, methyl siloxane bonded	SPB-5 fused silica capillary, 0.25 um 5% phenyl, methyl siloxane bonded	Chromosorb W-AW-DMCS (100/120 mesh) coated with 3% OV-17
Dimensions	30-m x 0.25-mm ID	30-m x 0.25-mm ID	1.8-m x 2-mm ID
Carrier Gas	Helium	Helium	Nitrogen
Carrier Gas Flow Rate	28-30 cm/sec (1 cm/minute)	28-30 cm/sec (1 cm/minute)	30-40 cm/minute
Column Program	35°C for 2 min; program at 8°C/min to 280°C and hold for 12 minutes	80°C for 2 min; program at 8°C/min to 280°C and hold for 12 minutes	Hold at 100°C for 4 minutes; program at 8°C/min to 280°C and hold for 15 minutes
Detector	Flame Ionization	Flame Ionization	Flame Ionization

(A) Without column cleanup (see Section 12.4)
(B) With column cleanup (see Section 12.4.1)

13.4 Prepare and calibrate the chromatographic system using either the external standard technique (Section 13.4.1) or the internal standard technique (Section 13.4.2). Figure 13.0 outlines the following sequence involving GC calibration and retention time window determination.

13.4.1 External Standard Calibration Procedure - For each analyte of interest, including surrogate compounds for spiking, if used, prepare calibration standards at a minimum of five concentration levels by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with methylene chloride. [Note: All calibration standards of interest involving selected PAHs, of the same concentration, can be prepared in the same flask.]

13.4.1.1 Prepare stock standard solutions at a concentration of 100 ug/uL by dissolving 0.100 gram of assayed PAH material in methylene chloride and diluting to vol- in a 10 mL volumetric flask. [Note: Larger volumes can be used at the convenience of the analyst.]

13.4.1.2 When compound purity is assayed to be 98% or greater, the weight can be used without correction to calculate the concentration of the stock standard. [Note: Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.] Transfer the stock standard solutions into Teflon®-sealed screw-cap bottles.

13.4.1.3 Store at 4°C and protect from light. Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Stock standard solutions must be replaced after one year, or sooner, if comparison with check standards indicates a problem.

13.4.1.4 Calibration standards at a minimum of five concentration levels should be prepared through dilution of the stock standards with methylene chloride. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. [Note: Calibration solutions must be replaced after six months, or sooner, if comparison with a check standard indicates a problem.]

13.4.1.5 Inject each calibration standard using the technique that will be used to introduce the actual samples into the gas chromatograph (e.g., 1- to 3-uL injections). [Note: The same amount must be injected each time.]

13.4.1.6 Tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each analyte. [Note: Alternatively, for samples that are introduced into the gas chromatograph using a syringe, the ratio of the response to the amount injected, defined as the calibration factor (CF), can be calculated for each analyte at each standard concentration by the following equation:

$$\text{Calibration factor (CF)} = \frac{\text{Total Area of Peak}}{\text{Mass injected (in nanograms)}}$$

If the percent relative standard deviation (%RSD) of the calibration factor is less than 20% over the working range, linearity through the origin can be assumed, and the average calibration factor can be used in place of a calibration curve.]

13.4.1.7 The working calibration curve or calibration factor must be verified on each working day by the injection of one or more calibration standards. If the response for any analyte varies from the predicted response by more than ±20%, a new calibration curve must be prepared for that analyte. Calculate the percent variance by the following equation:

$$\text{Percent variance} = \frac{R_2 - R_1}{R_1} \times 100$$

where

R_2 = Calibration factor from succeeding analysis.

R_1 = Calibration factor from first analysis.

13.4.2 Internal Standard Calilbration Procedure - To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Due to these limitations, no internal standard applicable to all samples can be suggested. [Note: It is recommended that the internal standard approach be used only when the GC/MS procedure is employed due to coeluting species.]

13.4.2.1 Prepare calibration standards at a minimum of five concentration levels for each analyte of interest by adding volumes of one or more stock standards to a volumetric flask.

13.4.2.2 To each calibration standard, add a known constant amount of one or more internal standard and dilute to volume with methylene chloride. [Note: One of the standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.]

13.4.2.3 Inject each calibration standard using the same introduction technique that will be applied to the actual samples (e.g., 1- to 3-uL injection).

13.4.2.4 Tabulate the peak height or area responses against the concentration of each compound and internal standard.

13.4.2.5 Calculate response factors (RF) for each compound as follows:

$$\text{Response Factor (RF)} = (A_s C_{is})/(A_{is} C_s)$$

where:

A_s = Response for the analyte to be measured (area units or peak height).

A_{is} = Response for the internal standard. (area units or peak height).

C_{is} = Concentration of the internal standard, (ug/L).

C_s = Concentration of the analyte to be measured, (ug/L).

13.4.2.6 If the RF value over the working range is constant (<20% RSD), the RF can be assumed to be invariant, and the average RF can be used for calculations. [Note: Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is} versus RF.]

13.4.2.7 The working calibration curve or RF must be verified on each working day by the measurement of one or more calibration standards.

13.4.2.8 If the response for any analyte varies from the predicted response by more than ±20%, a new calibration curve must be prepared for that compound.

13.5 Retention Time Windows Determination

13.5.1 Before analysis can be performed, the retention time windows must be established for each analyte.

13.5.2 Make sure the GC system is within optimum operating conditions.

13.5.3 Make three injections of the standard containing all compounds for retention time window determination. [Note: The retention time window must be established for each analyte throughout the course of a 72-hr period.]

13.5.4 The retention window is defined as plus or minus three times the standard deviation of the absolute retention times for each standard.

13.5.5 Calculate the standard deviation of the three absolute retention times for each single component standard. In those cases where the standard deviation for a particular standard is zero, the laboratory must substitute the standard deviation of a close eluting, similar compound to develop a valid retention time window.

13.5.6 The laboratory must calculate retention time windows for each standard on each GC column and whenever a new GC column is installed. The data must be noted and retained in a notebook by the laboratory as part of the user SOP and as a quality assurance check of the analytical system.

13.6 Sample Analysis

13.6.1 Inject 1- to 3-uL of the methylene chloride extract from Section 13.2 (however, the same amount each time) using the splitless injection technique when using capillary column. [Note: Smaller (1.0 uL) volumes can be injected if automatic devices are employed.]

13.6.2 Record the volume injected and the resulting peak size in area units or peak height.

13.6.3 Using either the internal or external calibration procedure, determine the identity and quantity of each component peak in the sample chromatogram through retention time window and established calibration curve. Table 2 outlines typical retention times for selected PAHs, using both the packed and capillary column technique coupled with FI detection, while Figure 14.0 illustrates typical chromatogram for a packed column analysis.

13.6.3.1 If the responses exceed the linear range of the system, dilute the extract and reanalyze. It is recommended that extracts be diluted so that all peaks are on scale. Overlapping peaks are not always evident when peaks are off scale. Computer reproduction of chromatograms, manipulated to ensure all peaks are on scale over a 100-fold range, are acceptable if linearity is demonstrated. Peak height measurements are recommended over peak area integration when overlapping peaks cause errors in area integration.

13.6.3.2 Establish daily retention time windows for each analyte. Use the absolute retention time for each analyte from Section 13.5.4 as the midpoint of the window for that day. The daily retention time window equals the midpoint ± three times the standard deviation determined in Section 13.5.4.

13.6.3.3 Tentative identification of an analyte occurs when a peak from a sample extract falls within the daily retention time window. [Note: Confirmation may be required on a second GC column, or by GC/MS (if concentration permits) or by other recognized confirmation techniques if overlap of peaks occur.]

13.6.3.4 Validation of GC system qualitative performance is performed through the use of the midlevel standards. If the mid-level standard falls outside its daily retention time window, the system is out of control. Determine the cause of the problem and perform a new calibration sequence (see Section 13.4).

13.6.3.5 Additional validation of the GC system performance is determined by the surrogate standard recovery. If the recovery of the surrogate standard deviates from 100% by not more than 20%, then the sample extraction, concentration, clean-up and analysis is certified. If it exceeds this value, then determine the cause of the problem and correct.

13.6.4 Determine the concentration of each analyte in the sample according to Sections 17.1 and 17.2.1.

14. Gas Chromatography with Mass Spectroscopy Detection

14.1 The analysis of the extracted sample for benzo[a]pyrene and other PAHs is accomplished by an electron impact gas chromatography/mass spectrometry (EI GC/MS) in the selected ion monitoring (SIM) mode with a total cycle time (including voltage reset time) of one second or less. The GC is equipped with an ultra No. 2 fused silica capillary column (50-m x 0.25-mm I.D.) with helium carrier gas for analyte separation. The GC column is temperature controlled and interfaced directly to the MS ion source.

14.2 The laboratory must document that the EI GC/MS system is properly maintained through periodic calibration checks. The GC/MS system should have the following specifications:

Mass range: 35-500 amu
Scan time: 1 sec/scan
GC Column: 50 m x 0.25 mm I.D. (0.25 um film thickness) Ultra No. 2 fused silica capillary column or equivalent
Initial column temperature and hold time: 40°C for 4 min
Column temperature program: 40-270°C at 10°C/min
Final column temperature hold: 270°C (until benzo[g,h,i] perylene has eluted)
Injector temperature: 250-300°C
Transfer line temperature: 250-300°C
Source temperature: According to manufacturer's specifications
Injector: Grob-type, splitless
EI Condition: 70 eV
Mass Scan: Follow manufacturer instruction for select ion monitoring (SIM) mode.
Sample volume: 1-3 uL
Carrier gas: Helium at 30 cm/sec.

The GC/MS is tuned using a 50 ng/uL solution of decafluorotriphenylphosphine (DFTPP). The DFTPP permits the user to tune the mass spectrometer on a daily basis. If properly tuned, the DFTPP key ions and ion abundance criteria should be met as outlined in Table 3.

14.3 The GC/MS operating conditions are outlined in Table 4. The GC/MS system can be calibrated using the external standard technique (Section 14.3.1) or the internal standard technique (Section 14.3.2). Figure 15.0 outlines the following sequence involving the GC/MS calibration.

14.3.1 External standard calibration procedure.

14.3.1.1 Prepare calibration standard of B[a]P or other PAHs at a minimum of five concentration levels by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with methylene chloride. The stock standard solution of B[a]P (1.0 ug/uL) must be prepared from pure standard materials or purchased as certified solutions.

14.3.1.2 Place 0.0100 grams of native B[a]P or other PAHs on a tared aluminum weighing disk and weigh on a Mettler balance.

14.3.1.3 Quantitatively, transfer to a 10 ml volumetric flask. Rinse the weighing disk with several small portions of methylene chloride. Ensure all material has been transferred.

14.3.1.4 Dilute to mark with methylene chloride.

14.3.1.5 The concentration of the stock standard solution of B[a]P or other PAHs in the flask is 1.0 ug/uL [Note: Commerically prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.]

14.3.1.6 Transfer the stock standard solutions into Teflon®-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

14.3.1.7 Stock standard solutions must be replaced after 1 yr or sooner if comparison with quality control check samples indicates a problem.

14.3.1.8 Calibration standards at a minimum of five concentration levels should be prepared. [Note: One of the calibration standards should be at a concentration near, but above the method detection limit; the others should correspond to the range of concenrations found in the sample but should not exceed the working range of the GC/MS system.] Accurately pipette 1.0 ml of the stock solution (1 ug/uL) into another 10 mL volumetric flask, dilute to mark with methylene chloride. This daughter solution contains 0.1 ug/uL of B[a]P or other PAHs.

14.3.1.9 Prepare a set of standard solutions by appropriately diluting, with methylene chloride, accurately measured volumes of the daughter solution (0.1 ug/uL).

14.3.1.10 Accurately pipette 100 uL, 300 uL, 500 uL, 700 uL and 1000 uL of the daughter solution (0.1 ug/uL) into each 10 mL volumetric flask, respectively. To each of these flasks, add an internal deuterated standard to give a final concentration of 40 ng/uL of the internal deuterated standard (Section 14.3.2.1). Dilute to mark with methylene chloride.

14.3.1.11 The concentration of B[a]P in each flask is 1 ng/uL, 3 ng/uL, 5 ng/uL, 7 ng/uL, and 10 ug/uL respectively. All standards should be stored at 4°C and protected from fluorescent light and should be freshly prepared once a week or sooner if check standards indicates a problem.

14.3.1.12 Analyze a constant volume (1-3 uL) of each calibration standard and tabulate the area responses of the primary characteristic ion of each standard against the mass injected. The results may be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to amount injected (calibration factor) is a constant over the working range (<20% relative standard deviation, RSD), linearity through the origin may be assumed and the average ratio or calibration factor may be used in place of a calibration curve.

14.3.1.13 The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ± 20%, the rest must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor must be prepared for that compound.

14.3.2 Internal standard calibration procedure.

14.3.2.1 To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. For analysis of B[a]P, the analyst should use perylene -d_{12}. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. The following internal standards are suggested at a concentration of 40 ng/uL for specific PAHs:

Perylene - d_{12}

Benzo(a)pyrene
Benzo(k)fluoranthene
Benzo(g,h,i)perylene
Dibenzo(a,h)anthracene
Indeno(1,2,3-cd)pyrene

Chrysene - d_{12}

Benzo(a)anthracene
Chrysene
Pyrene

Acenaphthene - d_{10}

Acenaphthene
Acenaphthylene
Fluorene

Naphthalene - d_8

Naphthalene

Phenanthrene -d_{10}

Anthracene
Fluoranthene
Phenanthrene

14.3.2.2 A mixture of the above deuterated compounds in the appropriate concentration range are commercially available (see Section 9.3.1.5).

14.3.2.3 Use the base peak ion as the primary ion for quantification of the standards. If interferences are noted, use the next two most intense ions as the secondary ions. The internal standard is added to all calibration standards and all sample extracts analyzed by GC/MS. Retention time standards, column performance standards, and a mass spectrometer tuning standard may be included in the internal standard solution used.

14.3.2.4 Prepare calibration standards at a minimum of three concentration level for each parameter of interest by adding appropriate volumes of one or more stock standards to a volumetric flask. To each calibration standard or standard mixture, add a known constant amount of one or more of the internal deuterated standards to yield a resulting concentration of 40 ng/uL of internal standard and dilute to volume with methylene chloride. One of the calibration standards should be at a concentration near, but above, the minimum detection limit (MDL) and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC/MS system.

14.3.2.5 Analyze constant amount (1-3 uL) of each calibration standard and tabulate the area of the primary characteristic ion against concentration for each compound and internal standard, and calculate the response factor (RF) for each analyte using the following equation:

$$RF = (A_s C_{is})/(A_{is} C_s)$$

Where:

A_s = Area of the characteristic ion for the analyte to be measured.

A_{is} = Area of the characteristic ion for the internal standard.

C_{is} = Concentration of the internal standard, (ng/uL).

C_s = Concentration of the analyte to be measured, (ng/uL).

If the RF value over the working range is a constant (<20% RSD), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is}, vs. RF. Table 5.0 outlines key ions for selected internal deuterated standards.

14.3.2.6 The working calibration curve or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ± 20%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared.

14.3.2.7 The relative retention times for each compound in each calibration run should agree within 0.06 relative retention time units.

14.4 Sample Analysis

14.4.1 It is highly recommended that the extract be screened on a GC/FID or GC/PID using the same type of capillary column as in the GC/MS procedure. This will minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds.

14.4.2 Analyze the 1 mL extract (see Section 13.2) by GC/MS. The recommended GC/MS operating conditions to be used are specified in Section 14.2.

14.4.3 If the response for any quantitation ion exceeds the initial calibration curve range of the GC/MS system, extract dilution must take place. Additional internal standard must be added to the diluted extract to maintain the required 40 ng/uL of each internal standard in the extracted volume. The diluted extract must be reanalyzed.

14.4.4 Perform all qualitative and quantitative measurements as described in Section 14.3. The typical characteristic ions for selective PAHs are outlined in Table 6.0. Store the extracts at 4°C, protected from light in screw-cap vials equipped with unpierced Teflon®-lined, for future analysis.

14.4.5 For sample analysis, the comparison between the sample and references spectrum must illustrate:

(1) Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within ±20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contaminatiuon or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

14.4.6 Determine the concentration of each analyte in the sample according to Sections 17.1 and 17.2.2.

14.5 GC/MS Performance Tests

14.5.1 Daily DFTPP Tuning - At the beginning of each day that analyses are to be performed, the GC/MS system must be checked to see that acceptable performance criteria are achieved when challenged with a 1 uL injection volume containing 50 ng of decafluorotriphenylphosphine (DFTPP). The DFTPP key ions and ion abundance criteria that must be met are illustrated in Table 3.0. Analysis should not begin until all those criteria are met. Background subtraction should be staightforward and designed only to eliminate column bleed or instrument background ions. The GC/MS tuning standard should also be used to assess GC column performance and injection port inertness. Obtain a background correction mass spectra of DFTPP and check that all key ions criteria are met. If the criteria are not achieved, the analyst must retune the mass spectromete and repeat the test until all criteria are achieved. The performance criteria must be achieved before any samples, blanks on standards are analyzed. If any key ion abundance observed for the daily DFTPP mass tuning check differs by more than 10% absolute abundance from that observed during the previous daily tuning, the instrument must be retuned or the sample and/or calibration solution reanalyzed until the above condition is met.

14.5.2 Daily 1-point Initial Calibration Check - At the beginning of each work day, a daily 1-point calibration check is performed by re-evaluating the midscale calibration standard. This is the same check that is applied during the initial calibration, but one instead of five working standards are evaluated. Analyze the one working standards under the same conditions the initial calibration curve was evaluated. Analyze 1 uL of each of the mid-scale calibration standard and tabulate the area response of the primary characteristic ion against mass injected. Calculate the percent difference using the following equation:

$$\% \text{ Difference} = \frac{RF_C - \overline{RF}_I}{\overline{RF}_I} \times 100$$

Where:

$\overline{RF}_I$ = average response factor from initial calibration using mid-scale standard.

RF_C = response factor from current verification check using mid-scale standard.

If the percent difference for the mid-scale level is greater than 10%, the laboratory should consider this a warning limit. If the percent difference for the mid-scale standard is less than 20%, the initial calibration is assumed to be valid. If the criterion is not met (<20% difference), then corrective action MUST be taken. [Note: Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system.] This check must be met before analysis begins. If no source of the problem can be determined after corrective action has been taken, a new five-point calibration MUST be generated. This criterion MUST be met before sample analysis begins.

14.5.3 12-hour Calibration Verification - A calibration standard at mid-level concentration containing B[a]P or other PAHs must be performed every twelve continuous hours of analysis. Compare the standard every 12-hours with the average response factor from the initial calibration. If the % difference for the response factor (see Section 14.5.2) is less than 20%, then the GC/MS system is operative within initial calibration values. If the criteria is not met (>20% difference), then the source of the problem must be determined and a new five-point curve MUST be generated.

14.5.4 Surrogate Recovery - Additional validation of the GC system performance is determined by the surrogate standard recovery. If the recovery of the surrogate standard deviates from 100% by not more than 20%, then the sample extraction, concentration, clean-up and analysis is certified. If it exceeds this value, then determine the cause of the problem and correct.

15. High Performance Liquid Chromatography (HPLC) Detection

15.1 Introduction

15.1.1 Detection of B[a]P by HPLC has also been a viable tool in recent years. The procedure outlined below has been written specifically for analysis of B[a]P by HPLC. However, by optimizing chromatographic conditions [(multiple detector fluorescence - excitation at 240 nm, emission at 425 nm; ultraviolet at 254 nm)] and varying the mobile phase composition through a gradient program, the following PAHs may also be quantitatified:

COMPOUND	DETECTOR[1]	COMPOUND	DETECTOR[1]
Acenaphthene	UV	Benzo(k)fluoranthene	FL
Acenaphthylene	UV	Dibenzo(a,h)anthracene	FL
Anthracene	UV	Fluoranthene	FL
Benzo(a)anthracene	FL	Fluorene	UV
Benzo(a)pyrene	FL	Indeno(1,2,3-cd)pyrene	FL
Benzo(b)fluoranthene	FL	Naphthalene	UV
Benzo[e]pyrene	FL	Phenanthrene	UV
Benzo(ghi)perylene	FL	Pyrene	FL

[1] UV= Ultraviolet
FL= Fluorescences

15.1.2 This method provides quantitative identification of the selected PAH's compounds listed above by high performance liquid chromatography. It is based on separating of compounds of a liquid mixture through a liquid chromatographic column and measuring the separated components with suitable detectors.

15.1.3 The method involves solvent exchange, with subsequent HPLC detection involving ultraviolet (UV) and fluoresence (FL) detection.

15.2 Solvent Exchange To Acetonitrile

15.2.1 To the extract in the concentrator tube, add 4 mL of acetonitrile and a new boiling chip; attach a micro-snyder column to the apparatus.

15.2.2 Increase temperature of the hot water bath to 95 to 100°C.

15.2.3 Concentrate the solvent as in Section 12.3.

15.2.4 After cooling, remove the micro-Snyder column and rinse its lower sections into the concentration tube with approximately 0.2 mL acetonitrile.

15.2.5 Adjust its volume to 1.0 mL.

15.3 HPLC Assembly

15.3.1 The HPLC system is assembled, as illustrated in Figure 10.

15.3.2 The HPLC system is operated according to the following parameters:

HPLC Operating Parameters

Guard Column: VYDAC 201 GCCIOYT
Analytical Column: VYDAC 201 TP5415 C-18 RP (0.46 x 25 cm)
Column Temperature: 27.0 ± 2°C
Mobile Phase:

Solvent Composition	Time (Minutes)
40% Acetonitrile/60% water	0
100% Acetonitrile	25
100% Acetonitrile	35
40% Acetonitrile/60% water	45

Linear gradient elution at 1.0 mL/min
Detector: Variable wavelength ultraviolet and fluorescence.
Flow Rate: 1.0 mL/minute

[Note: To prevent irreversible absorption due to "dirty" injections and premature loss of column efficiency, a guard column is installed between the injector and the analytical column. The guard column is generally packed with identical material as is found in the analytical column. The guard column is generally replaced with a fresh guard column after several injections (50) or when separation between compounds becomes difficult. The analytical column specified in this procedure has been laboratory evaluated. Other analytical columns may be used as long as they meet procedure and separation requirements. Table 7.0 outlines other columns uses to determine PAHs by HPLC.]

15.3.3 The mobile phases are placed in separate HPLC solvent reservoirs and the pumps are set to yield a total of 1.0 mL/minute and allowed to pump for 20-30 minutes before the first analysis. The detectors are switched on at least 30 minutes before the first analysis. UV detection at 254 nm is generally preferred. The fluorescence spectrometer excitation wavelengths range from 250 to 800 nanometers. The excitation and emission slits are both set at 10 nanometers nominal bandpass.

15.3.4 Before each analysis, the detector baseline is checked to ensure stable operation.

15.4 HPLC Calibration

15.4.1 Prepare stock standard solutions at PAH concentrations of 1.00 ug/uL by dissolving 0.0100 grams of assayed material in acetonitrile and diluting to volume in a 10 mL volumetric flask. [Note: Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 98% or greater, the weight can be used without correction to calculate the concentration of the stock standard.] Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

15.4.2 Transfer the stock standard solutions into Teflon®-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

15.4.3 Stock standard solutions must be replaced after one year, or sooner, if comparision with check standards indicates a problem.

15.4.4 Prepare calibration standards at a minimum of five concentration levels ranging from 1 ng/uL to 10 ng/uL by first diluting the stock standard 10:1 with acetonitrile, giving a daughter solution of 0.1 ug/uL. Accurately pipette 100 uL, 300 uL, 500 uL, 700 uL and 1000 uL of the daughter solution (0.1 ug/uL) into each 10 mL volumetric flask, respectively. Dilute to mark with acetonitrile. One of the concentration levels should be at a concentration near, but above, the method detection limit (MDL). The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the HPLC. [Note: Calibration standards must be replaced after six months, or sooner, if comparison with check standards indicates a problem.]

15.4.5 Analyze each calibration standard (at lease five levels) three times. Tabulate area response vs. mass injected. All calibration runs are performed as described for sample analysis in Section 15.5.1. Typical retetion times for specific PAHs are illustrated in Table 8.0. Linear response is indicated where a correlation coefficient of at least 0.999 for a linear least-squares fit of the data (concentration versus area response) is obtained. The retention times for each analyte should agree within ± 2%.

15.4.6 Once linear response has been documented, an intermediate concentration standard near the anticipated levels for each component, but at least 10 times the detection limit, should be chosen for a daily calibration check. The response for the various components should be within 15% day to day. If greater variability is observed, recalibration may be required or a new calibration curve must be developed from fresh standards.

15.4.7 The response for each component in the daily calibration standard is used to calculate a response factor according to the following equation:

$$RF_C = \frac{C_C \times V_I}{R_C}$$

Where

RF_C = response factor (usually area counts) for the component of interest in nanograms injected/response unit.

C_C = concentration (mg/L) of analyte in the daily calibration standard.

V_I = volume (uL) of calibration standard injected.

R_C = response (area counts) for analyte in the calibration standard.

15.5 Sample Analysis

15.5.1 A 100 uL aliquot of the sample is drawn into a clean HPLC injection syringe. The sample injection loop (10 uL) is loaded and an injection is made. The data system, if available, is activated simultaneously with the injection and the point of injection is marked on the strip-chart recorded.

15.5.2 After approximately one minute, the injection valve is returned to the "load" position and the syringe and valve are flushed with water in preparation for the next sample analysis.

15.5.3 After elution of the last component of interest, concentrations are calculated as described in Section 16.2.3. [Note: Table 8.0 illustrates typical retention times associates with individual PAHs, while Figure 17 represent a typical chromatogram associates with fluorescence detection.]

15.5.4 After the last compound of interest has eluted, establish a stable baseline; the system can be now used for further sample analyses as described above.

15.5.5 If the concentration of analyte exceeds the linear range of the instrument, the sample should be diluted with mobile phase, or a smaller volume can be injected into the HPLC.

15.5.6 Calculate surrogate standard recovery on all samples, blanks and spikes. Calculate the percent difference by the following equation:

$$\% \text{ difference} = \frac{S_R - S_I}{S_I} \times 100$$

Where

S_I = surrogate injected, ng.
S_R = surrogate recovered, ng.

15.5.7 Once a minimum of thirty samples of the same matrix have been analyzed, calculte the averge percent recovery (%R) and standard deviation of the percent recovery (SD) for the surrogate.

15.5.8 For a given matrix, calculate the upper and lower control limit for method performance for the surrogate standard. This should be done as follows:

Upper Control Limit (UCL) = (%R) + 3(SD)

Lower Control Limit (LCL) = (%R) - 3(SD)

The surrogate recovery must fall within the control limits. If recovery is not within limits, the following is required.

- Check to be sure there are no errors in calculations surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

15.5.9 Determine the concentration of each analyte in the sample according to Sections 17.1 and 17.2.3.

15.6 HPLC System Performance

15.6.1 The general appearance of the HPLC system should be similar to that illustrated in Figure 10.

15.6.2 HPLC system efficiency is calculated according to the following equation:

$$N = 5.54 \quad \frac{t_r^{\;2}}{W_{1/2}}$$

where:

N = column efficiency (theoretical plates).

t_r = retention time (seconds) of analyte.

$W_{1/2}$ = width of component peak at half height (seconds).

A column efficiency of >5,000 theoretical plates should be obtained.

15.6.3 Precision of response for replicate HPLC injections should be $\pm 10\%$ or less, day to day, for analyte calibration standards at 1 ug/mL or greater levels. At 0.5 ug/mL level and below, precision of replicate analyses could vary up to 25%. Precision of retention times should be $\pm 2\%$ on a given day.

15.6.4 From the calibration standards, area responses for each PAH compound can be used against the concentrations to establish working calibration curves. The calibration curve must be linear and have a correlation coefficient greater than 0.98 to be acceptable.

15.6.5 The working calibration curve should be checked daily with an analysis of one or more calibration standards. If the observed response (r_p) for any PAH varies by more than 15% from the predicted response (r_p), the test method must be repeated with new calibration standards. Alternately a new calibration curve must be prepared. [Note: If $\frac{r_o - r_p}{r_p}$ >15%, recalibration is necessary.]

15.7 HPLC Method Modification

15.7.1 The HPLC procedure has been automated by Acurex Corporation as part of their "Standard Operating Procedure for Polynuclear Aromatic Hydrocarbon Analysis by High Performance Liquid Chromatography Methods," as reported in Reference 9 of Section 18.

15.7.2 The system consists of a Spectra Physics 8100 Liquid Chromatograph, a micro-processor-controlled HPLC, a ternary gradient generator, and an autosampler (10 uL injection loop).

15.7.3 The chromatographic analysis involves an automated solvent program allowing unattended instrument operation. The solvent program consists of four timed segments using varying concentrations of acetonitrile in water with a constant flow rate, a constant column temperature, and a 10-minute equilibration time, as outlined below.

AUTOMATED HPLC WORKING PARAMETERS

Time	Solvent Composition	Temperature	Rate
10 minutes equilibration	40% Acetonitrile 60% Water	27.0 ± 2°C	1 mL/min
T=0	40% Acetonitrile 60% Water		
T=25	100% Acetonitrile		
T=35	100% Acetonitrile		
T=45	40% Acetonitrile 60% Water		

Table 9.0 outlines the associated PAHs with their minimum detection limits (MDL) which can be detected employing the automated HPLC methodology.

15.7.4 A Vydac or equivalent analytical column packed with a C_{18} bonded phase is used for PAH separation with a reverse phase guard column. The optical detection system consists of a Spectra Physics 8440 variable Ultraviolet (UV)/Visible (VIS) wavelength detector and a Perkin Elmer LS-4 Fluorescence Spectrometer. The UV/VIS detector, controlled by remote programmed commands, contains a Deuterium lamp with wavelength selection between 150 and 600 nanometers. It is set at 254 nanometers with the time constant (detector response) at 1.0 seconds.

15.7.5 The LS-4 Fluorescence Spectrometer contains separate excitation and emission monochromators which are positioned by separate microprocessor-controlled stepper motors. It contains a Xenon discharge lamp, side-on photomultiplier and a 3-microliter illuminated volume flow cell. It is equipped with a wavelength programming facility to set the monochromators automatically to a given wavelength position. This greatly enhances selectivity by changing the fluorescence excitation and emission detection wavelengths during the chromatographic separation in order to optimize the detection of each PAH. The excitation wavelengths range from 230 to 720 nanometers; the emission wavelengths range from 250 to 800 nanometes. The excitation and emission slits are both set at 10 nanometers nominal bandpass.

15.7.6 The UV detector is used for determining naphthalene, acenapthylene and acenapthene, and the fluorescence detector is used for the remaining PAHs. Table 9 outlines the detection techniques and minimum detection limit (MDL) employing this HPLC system. A Dual Channel Spectra Physics (SP) 4200 computing integrator, with a Labnet power supply, provides data analysis and a chromatogram. An IBM PC XT with a 10-megabyte hard disk provides data storage and reporting. Both the SP4200 and the IBM PC XT can control all functions of the instruments in the series through the Labnet system except for the LS-4, whose wavelength program is started with a signal from the High Performance Liquid Chromatograph autosampler when it injects. All data are transmitted to the XT and stored on the hard disk. Data files can later be transmitted to floppy disk storage.

16.0 Quality Assurance/Quality Control

16.1 General System QA/QC

16.1.1 Each laboratory that uses these methods is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document quality data. The laboratory must maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate a typical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

16.1.2 Before processing any samples, the analyst should demonstrate, through the analysis of a reagent solvent blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is extracted or there is a change in reagents, a reagent solvent blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement steps.

16.1.3 For each analytical batch (up to 20 samples), a reagent blank, matrix spike and deuterated/surrogate samples must be analyzed (the frequency of the spikes may be different for different monitoring programs). The blank and spiked samples must be carried through all stages of the sample preparation and measurement steps.

16.1.4 The experience of the analyst performing gas chromatography and high performance liquid chromatography is invaluable to the success of the methods. Each day that analysis is performed, the daily calibration sample should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal?; Is the response windows obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still good, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g., column changed), recalibration of the system must take place.

16.2 Process, Field, and Solvent Blanks

16.2.1 One cartridge (XAD-2 or PUF) and filter from each batch of approximately twenty should be analyzed, without shipment to the field, for the compounds of interest per to serve as a process blank. A blank level of less than 10 ng per cartridge/filter assembly for single PAH component is considered to be acceptable.

16.2.2 During each sampling episode, at least one cartridge and filter should be shipped to the field and returned, without drawing air through the sampler, to serve as a field blank.

16.2.3 During the analysis of each batch of samples at least one solvent process blank (all steps conducted but no cartridge or filter included) should be carried through the procedure and analyzed. Blank levels should be less than 10 ng/sample for single components to be acceptable.

16.2.4 Because the sampling configuration (filter and backup adsorbent) has been tested for targeted PAHs in the laboratory in relationship to collection efficiency and has been demonstrated to be greater than 95% for targeted PAHs, no field recovery evaluation will occur as part of the QA/QC program outlined in this section.

16.3 Gas Chromatography with Flame Ionization Detection

16.3.1 Under the calibration procedures (internal and external), the % RSD of the calibration factor should be <20% over the linear working range of a five point calibration curve (Sections 13.4.1.6 and 13.4.2.6).

16.3.2 Under the calibration procedures (internal and external), the daily working calibration curve for each analyte should not vary from the predicted response by more than ±20% (Sections 13.4.1.7 and 13.4.2.8).

16.3.3 For each analyte, the retention time window must be established (Section 13.5.1), verified on a daily basis (Section 13.6.3.2) and established for each analyte throughout the course of a 72-hour period (Section 13.5.3).

16.3.4 For each analyte, the mid-level standard must fall within the retention time window on a daily basis as a qualitative performance evaluation of the GC system (Section 13.6.3.4).

16.3.5 The surrogate standard recovery must not deviate from 100% by no more than 20% (Section 13.6.3.5).

16.4 Gas Chromatography with Mass Spectroscopy Detection

16.4.1 Section 14.5.1 requires the mass spectrometer be tuned daily with DFTPP and meet relative ion abundance requirements outlined in Table 3.

16.4.2 Section 14.3.1.1 requires a minimum of five concentration levels of each analyte (plus deuterated internal standards) be prepared to establish a calibration factor to illustrate <20% variance over the linear working range of the calibration curve.

16.4.3 Section 14.3.1.13 requires the verification of the working curve each working day (if using the external standard technique) by the measurement of one or more calibration standards. The predicted response must not vary by more than ±20%.

16.4.4 Section 14.3.2.6 requires the initial calibration curve be verified each working day (if using the internal standard technique) by the measurement of one or more calibration standards. If the response varies by more than ±20% of predicted response, a fresh calibration curve (five point) must be established.

16.4.5 Section 14.4.5 requires that for sample analysis, the comparison between the sample and reference spectrum illustrate:

(1) Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within ±20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

(3) Molecular ions present in the reference spectrum should be present in sample the spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contaminatiuon or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

16.4.6 Section 14.5.3 requires that initial calibration curve be verified every twelve continuous hour of analysis by a mid-level calibration standard. The response must be less than 20% difference from the initial response.

16.4.7 The surrogate standard recovery must not deviate from 100% by no more than 20% (Section 14.5.4).

16.5 High Performance Liquid Chromatography

16.5.1 Section 15.4.4 requires the preparation of calibration standards at a minimum of five concentration levels to establish correlation coefficient of at least 0.999 for a linear least-squares fit of the data.

16.5.2 Section 15.4.5 requires that the retention time for each analyte should agree within ±2%.

16.5.3 A daily calibration check involving an intermediate standard of the initial five point calibration curve should be within ±15% from day to day.

16.5.4 Section 15.5.6 requires the calculation of percent difference of surrogate standard recovery in order to establish control limits:

Upper Control Limit (UCL) = (%R) + 3 (SD)
Lower Control Limit (LCL) = (%R) - 3 (SD)

The surrogate recovery must fall within the control limits.

17. Calculations

17.1 Sample Volume

17.1.1 The total sample volume should be corrected to standard temperature and pressure.

17.1.2 The total sample volume (V_m) is calculated from the periodic flow readings (Magnehelic readings taken in Section 11.3.13) using the following equation.

$$V_m = \frac{Q_1 + Q_2 \ldots O_n}{N} \times \frac{T}{1000}$$

Where

V_m = total sample volume (m^3) at ambient conditions .

$Q_1, Q_2 \ldots Q_n$ = flow rates determined at the beginning, end, and intermediate points during sampling (m3/minute).

N = number of data points.

T = elapsed sampling time (minutes).

17.1.3 The volume of air sampled can be converted to standard conditions (760 mm Hg pressure and 25°C) using the following equation:

$$V_s = V_m \times \frac{p_A}{760} \times \frac{298}{273 + t_A}$$

Where

V_s = total sample volume (m^3) at standard temperature and pressure (25°C and 760 mm Hg pressure).

V_m = total sample flow under ambient conditions (m^3).

p_A = ambient pressure (mm Hg).

t_A = ambient temperature (°C).

17.2 Sample Concentration

17.2.1 GC/FI Detection

17.2.1.1 The concentration of each analyte in the sample may be determined from the external standard technique by calculating the amount of standard injected, from the peak response, using the calibration curve or the calibration factor determined in Section 13.4.1.6.

17.2.1.2 The concentration of a specific analyte is calculated as follows:

$$\text{Concentration, ng/m}^3 = \frac{[(A_x)(V_t)(D)]}{[(CF)(V_i)(V_s)]}$$

Where:

CF = calibration factor for chromatographic system, peak height or area response per mass injected, Section 13.4.1.6.

A_x = Response for the analyte in the sample, area counts or peak height.

V_t = volume of total sample, uL.

D = Dilution factor, if dilution was made on the sample prior to analysis. If no dilution was made, D=1, dimensionless.

V_i = volume of sample injected, uL

V_s = total sample volume (m^3) at standard temperature and pressure (25°C and 760 mm Hg), Section 17.1.3.

17.2.2 GC/MS Detection

17.2.2.1 When an analyte has been identified, the quantification of that analyte will be based on the integrated abundance from the monitoring of the primary characteristic ion. Quantification will take place using the internal standard technique. The internal standard used shall be the one nearest the retention time of that of a given analyte (see Section 14.3.2.1).

17.2.2.2 Calculate the concentration of each identified analyte in the sample as follows:

$$\text{Concentration, ng/m}^3 = \frac{[(A_x)(I_s)(V_t)(D)]}{[(A_{is})(RF)(V_i)(V_s)]}$$

Where

A_x = area of characteristic ion(s) for analyte being measured.

I_s = amount of internal standard injected, ng.

V_t = volume of total sample, uL.

D = dilution factor, if dilution was made on the sample prior to analysis. If no dilution was made, D = 1, dimensionless.

A_{is} = area of characteristic ion(s) for internal standard.

RF = Response factor for analyte being measured, Section 14.3.2.5.

V_i = volume of analyte injected, uL.

V_s = total sample volume (m^3) at standard temperature and pressure (25°C and 760 mm Hg), Section 17.1.3.

17.2.3 HPLC Detection

17.2.3.1 The concentration of each analyte in the sample may be determined from the external standard technique by calculating response factor and peak response using the calibration curve.

17.2.3.2 The concentration of a specific analyte is calculated as follows:

$$\text{Concentration, ng/m}^3 = \frac{[(RF_c)(A_x)(V_t)(D)]}{[(V_i)(V_s)]}$$

Where

RF_c = response factor (nanograms injected per area counts) calculated in Section 15.4.7.

A_x = response for the analyte in the sample, area counts or peak height.

V_t = volume of total sample, uL.

D = dilution factor, if dilution was made on the sample prior to analysis. If no dilution was made, D = 1, dimensionless.

V_i = volume of sample injected, uL.

V_s = total sample volume (m^3) at standard temperature and pressure (25°C and 760 mm Hg), Section 17.1.3.

17.3 Sample Concentration Conversion From ng/m^3 to ppbv

17.3.1 The concentrations calculated in Section 17.2 can be converted to ppbv for general reference.

17.3.2 The analyte concentration can be converted to ppbv using the following equation:

$$C_A\ (\text{ppbv}) = C_A\ (\text{ng/m}^3) \times \frac{24.4}{MW_A}$$

Where

C_A = concentration of analyte, ng/m^3, calculated according to Sections 17.2.1 through 17.2.3.

MW_A = molecular weight of analyte, g/g-mole

24.4 = molar volume occupied by ideal gas at standard temperature and pressure (25°C and 760 mm Hg), l/mole.

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TABLE 1.0 FORMULAE AND PHYSICAL PROPERTIES OF SELECTIVE PAHs

	FORMULA	MOLECULAR WEIGHT	MELTING POINT °C	BOILING POINT °C	CASE #
Acenaphthene	$C_{12}H_{10}$	154.21	96.2°	279	83-32-9
Acenaphthylene	$C_{12}H_8$	152.20	92-93	265-275	208-96-8
Anthracene	$C_{14}H_{10}$	178.22	218°	342	120-12-7
Benzo(a)anthracene	$C_{18}H_{12}$	228.29	158-159	-	56-55-3
Benzo(a)pyrene	$C_{20}H_{12}$	252.32	177°	310-312	50-32-8
Benzo(b)fluoranthene	$C_{20}H_{12}$	252.32	168	-	205-99-2
Benzo(e)pyrene	$C_{20}H_{12}$	252.32	178-179	-	192-92-2
Benzo(g,h,i)perlene	$C_{22}H_{12}$	276.34	273	-	191-24-2
Benzo(k)fluoranthene	$C_{20}H_{12}$	252.32	217	480	207-08-9
Chrysene	$C_{18}H_{12}$	228.29	255-256	-	218-01-9
Dibenzo(a,h)anthracene	$C_{22}H_{14}$	278.35	262	-	53-70-3
Fluoranthene	$C_{16}H_{10}$	202.26	110	-	206-44-0
Fluorene	$C_{13}H_{10}$	166.22	116-117	293-295	86-73-7
Indeno(1,2,3-cd)pyrene	$C_{22}H_{12}$	276.34	161.5-163	-	193-39-5
Naphthalene	$C_{10}H_8$	128.16	80.2	217.9	91-20-3
Phenanthrene	$C_{14}H_{10}$	178.22	100°	340	85-01-8
Pyrene	$C_{16}H_{10}$	202.26	156	399	129-00-0

*Many of these compounds sublime.

TABLE 2.0 RETENTION TIMES FOR SELECTIVE PAHs FOR PACKED AND CAPILLARY COLUMNS

Compound	Packed[1]	Capillary[2]
Acenaphthene	10.8	16.8
Acenaphthylene	10.4	15.9
Anthracene	15.9	20.7
Benzo(a)anthracene	20.6	29.1
Benzo(a)pyrene	29.4	36.2
Benzo(b)fluoranthene	28.0	34.2
Benzo(ghi)perylene	38.6	48.4
Benzo(k)fluoranthene	28.0	34.4
Chrysene	24.7	29.3
Dibenzo(a,h)anthracene	36.2	46.1
Fluoranthene	19.8	24.3
Fluorene	12.6	18.1
Indeno(1,2,3-cd)pyrene	36.2	45.6
Naphthalene	4.5	11.0
Phenanthrene	15.9	20.6
Pyrene	20.6	25.0

[1] GC conditions: Chromosorb W-AW-DMCS (100/120 mesh) coated with 3% OV-17, packed in a 1.8-m long x 2 mm ID glass column, with nitrogen carrier gas at a flow rate of 40 mL/min. Column temperature was held at 100°C for 4 min. then programmed at 8°/minute to a final hold at 280°C.

[2] Capillary GC conditions: 30 meter fused silica SPB-5 capillary column; flame ionization detector, splitless injection; oven temperature held at 80 degrees C for 2 minutes, increased at 8 degrees/min. to 280 degrees C.

TABLE 3.0 DFTPP KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
51	30-60% of mass 198
68	Less than 2% of mass 69
70	Less than 2% of mass 69
127	40-60% of mass 198
197	Less than 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	Greater than 1% of mass 198
441	Present but less than mass 443
442	Greater than 40% of mass 198
443	17-23% of mass 442

TABLE 4.0 GC AND MS OPERATING CONDITIONS

Chromatography	
Column	Hewlett-Packard Ultra #2 crosslinked 5% phenyl methyl silicone (50 m x 0.25 mm, 0.25 um film thickness) or equivalent
Carrier Gas	Helium velocity 20 cm^3/sec at 250°C
Injection Volume	Constant (1-3 uL)
Injection Mode	Splitless
Temperature Program	
Initial Column Temperature	45°C
Initial Hold Time	1 min
Program	45°C to 100°C in 5 min, then 100°C to 320°C at 8°C/min
Final Hold Time	15 min
Mass Spectrometer	
Detection Mode	Multiple ion detection, SIM mode

TABLE 5.0 CHARACTERISTIC IONS FROM GC/MS DETECTION FOR DEUTERATED INTERNAL STANDARDS AND SELECTED PAHs

Compound	M/Z
D_8-naphthalene	136
D_{10}-phenanthrene	188
Phenathrene	178
Anthracene	178
Fluoranthene	202
D_{10}-pyrene	212
Pyrene	202
Cyclopenta[c,d]pyrene	226
Benz[a]anthracene	228
D_{12}-chrysene	240
Benzo[e]pyrene	252
D_{12}-benzo[a]pyrene	264
Benzo[a]pyrene	252

TABLE 6.0 CHARACTERISTIC IONS FROM GC/MS DETECTION FOR SELECTED PAHs

Compound	Primary		Secondary
Acenaphthene	154	153	152
Acenaphthylene	152	151	153
Anthracene	178	179	176
Benzo(a)anthracene	228	229	226
Benzo(a)pyrene	252	253	125
Benzo(b)fluoranthene	252	253	125
Benzo(ghi)perylene	276	138	277
Benzo(k)fluoranthene	252	253	125
Chrysene	228	226	229
Dibenzo(a,h)anthracene	278	139	279
Fluoranthene	202	101	203
Fluorene	166	165	167
Indeno(1,2,3-cd)pyrene	276	138	227
Naphthalene	128	129	127
Phenanthrene	178	179	176
Pyrene	202	200	203

TABLE 7.0. COMMERCIAL AVAILABLE COLUMNS FOR PAH ANALYSIS USING HPLC

Company	Column Identification	Column Name
The Separation Group P.O. Box 867 Hesperia, California 92345	201-TP	VYDAC
Rainin Instrument Company Mack Road Wasurn, MA 01801-4626	Ultrasphere - ODS	ALEX
Supelco, Inc. Supelco Park Bellefonte, PA 16823-0048	LC-PAH	Supelcosil
DuPont Company Biotechnology Systems Barley Mill Plaza, P24 Wilmington, DE 19898	ODS	Zorbax
Perkin-Elmer Corp. Corporate Office Main Avenue Norwalk, CT 06856	HC-ODS	Sil-X
Waters Associates 34-T Maple St. Milford, MA 01757	u-Bondapak	NH_3 u-Bondapak

TABLE 8.0. TYPICAL RETENTION TIME FOR SELECTIVE PAHs BY HPLC SEPARATION AND DETECTION

Compound	Retention Times (minutes) HPLC Conditions			
	Condition A Fluorescence	Condition A UV	Condition B Fluorescence	Condition B UV
Acenaphthene		20.5		18.0
Acenaphthylene		18.5		15.8
Anthracene	23.4		21.0	21.0
Benzo(a)anthracene	28.5		26.3	26.3
Benzo(a)pyrene	33.9		31.1	31.1
Benzo(b)fluoranthene	31.6		29.3	29.3
Benzo(e)pyrene			31.1	
Benzo(ghi)perylene	36.3		33.9	33.9
Benzo(k)fluoranthene	32.9		30.2	30.2
Chrysene	29.3		26.7	
Dibenzo(a,h)anthracene	35.7		32.7	32.7
Fluoranthene	24.5		22.5	22.5
Fluorene		21.2	18.5	18.5
Indeno(1,2,3-cd)pyrene	37.4		34.6	34.6
Naphthalene		16.6		14.0
Phenanthrene	22.1		19.9	19.9
Pyrene	25.4		23.4	23.4

Condition A HPLC parameters: Reverse phase HC-ODS Sil-X, 5 micron particle size, in a 250-mm x 2.6-mm I.D. stainless steel column. Isocratic elution for 5 min using acetonitrile/water (4:6)(v/v), then linear gradient elution to 100% acetonitrile over 25 min at 0.5 mL/min flow rate. If columns having other internal diameters are used, the flow rate should be adjusted to maintain a linear velocity of 2 mm/sec.

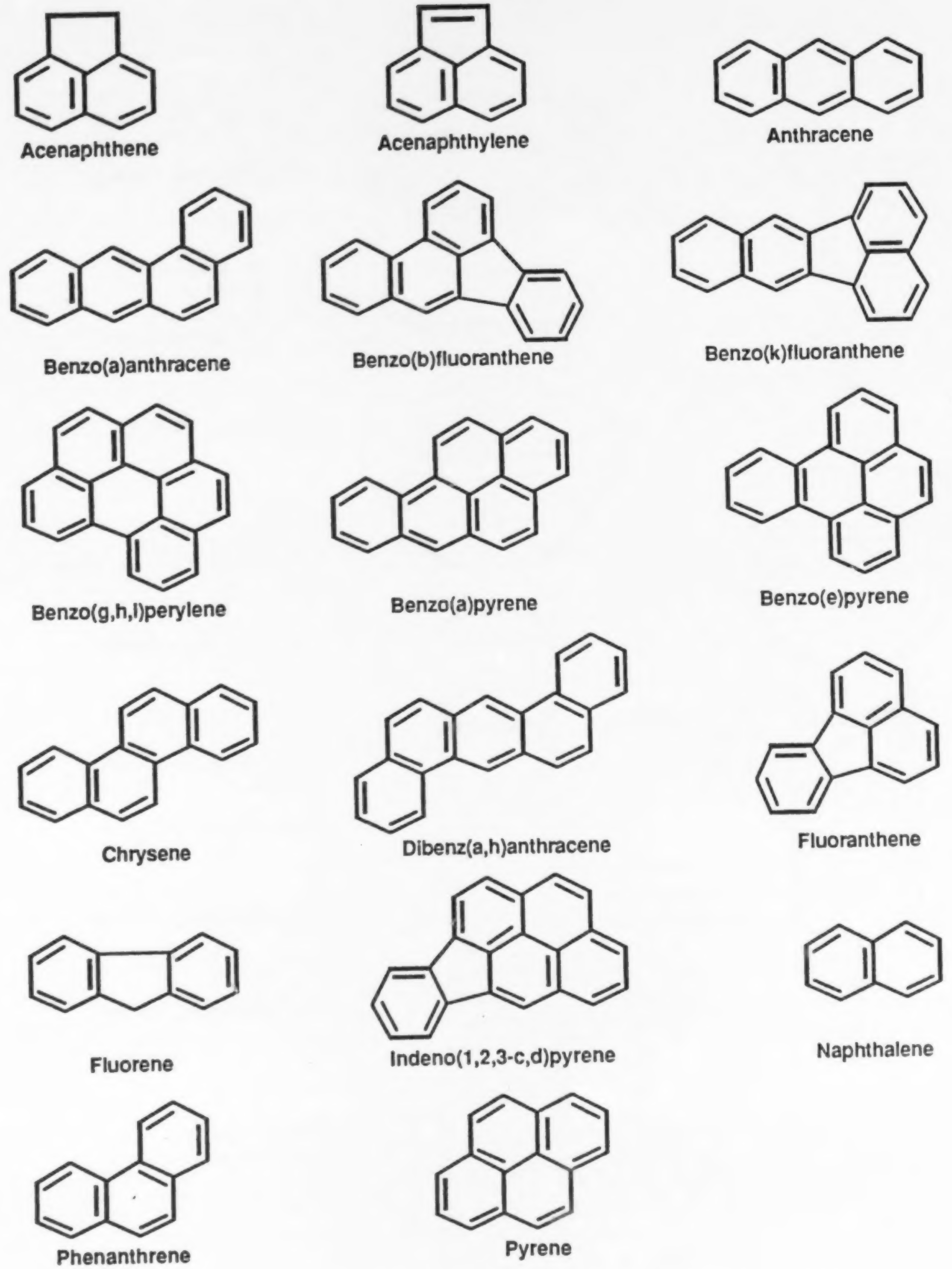
Condition B HPLC parameters: Reverse phase VYDAC 201 TP 5415, 5 micron particle size, in a .46 x 25 cm stainless steel column. Isocratic elution for 10 min using acetonitrile/water (4:6)(v/v), then linear gradient elution to 100% acetonitrile for 10 minutes then linear gradient to 40/60 acetonitrile for 10 minutes at 15 mL/min.

TABLE 9.0. RETENTION TIMES (RT) AND MINIMUM DETECTION LIMITS (MDLs) FOR SELECTED PAHs USING ULTRAVIOLET AND FLOURESCENCE DETECTION

	Ultraviolet Detector		Flourescence Detector	
PAH	RT	MDL	RT	MDL
Naphthalene	14.0	250pg/uL		
Acenaphthylene	15.85	250pg/uL		
Acenaphthene	18.0	250pg/uL		
Fluorene	18.5	50pg/uL	18.5	5pg/uL
Phenanthrene	19.9	50pg/uL	19.9	10pg/uL
Anthracene	21.0	50pg/uL	21.0	50pg/uL
Fluoranthene	22.5	50pg/uL	22.5	10pg/uL
Pyrene	23.4	50pg/uL	23.4	5pg/uL
Benzo(a)anthracene	26.3	50pg/uL	26.3	5pg/uL
Chrysene	26.7	50pg/uL	26.7	5pg/uL
Benzo(b)fluoranthene	29.3	50pg/uL	29.3	10pg/uL
Benzo(k)fluoranthene	30.2	50pg/uL	30.2	5pg/uL
Benzo(a)pyrene	31.1	50pg/uL	31.1	5pg/uL
Dibenzo(a,h)anthracene	32.7	50pg/uL	32.7	5pg/uL
Benzo(ghi)perylene	33.9	50pg/uL	33.9	5pg/uL
Indeno(1,2,3-cd)pyrene	34.6	50pg/uL	34.6	50pg/uL

RT = Retention time in minutes

MDL = Minimum detection limit



Acenaphthene

Acenaphthylene

Anthracene

Benzo(a)anthracene

Benzo(b)fluoranthene

Benzo(k)fluoranthene

Benzo(g,h,l)perylene

Benzo(a)pyrene

Benzo(e)pyrene

Chrysene

Dibenz(a,h)anthracene

Fluoranthene

Fluorene

Indeno(1,2,3-c,d)pyrene

Naphthalene

Phenanthrene

Pyrene

FIGURE 1.0 RING STRUCTURE OF SELECTIVE PAHs.

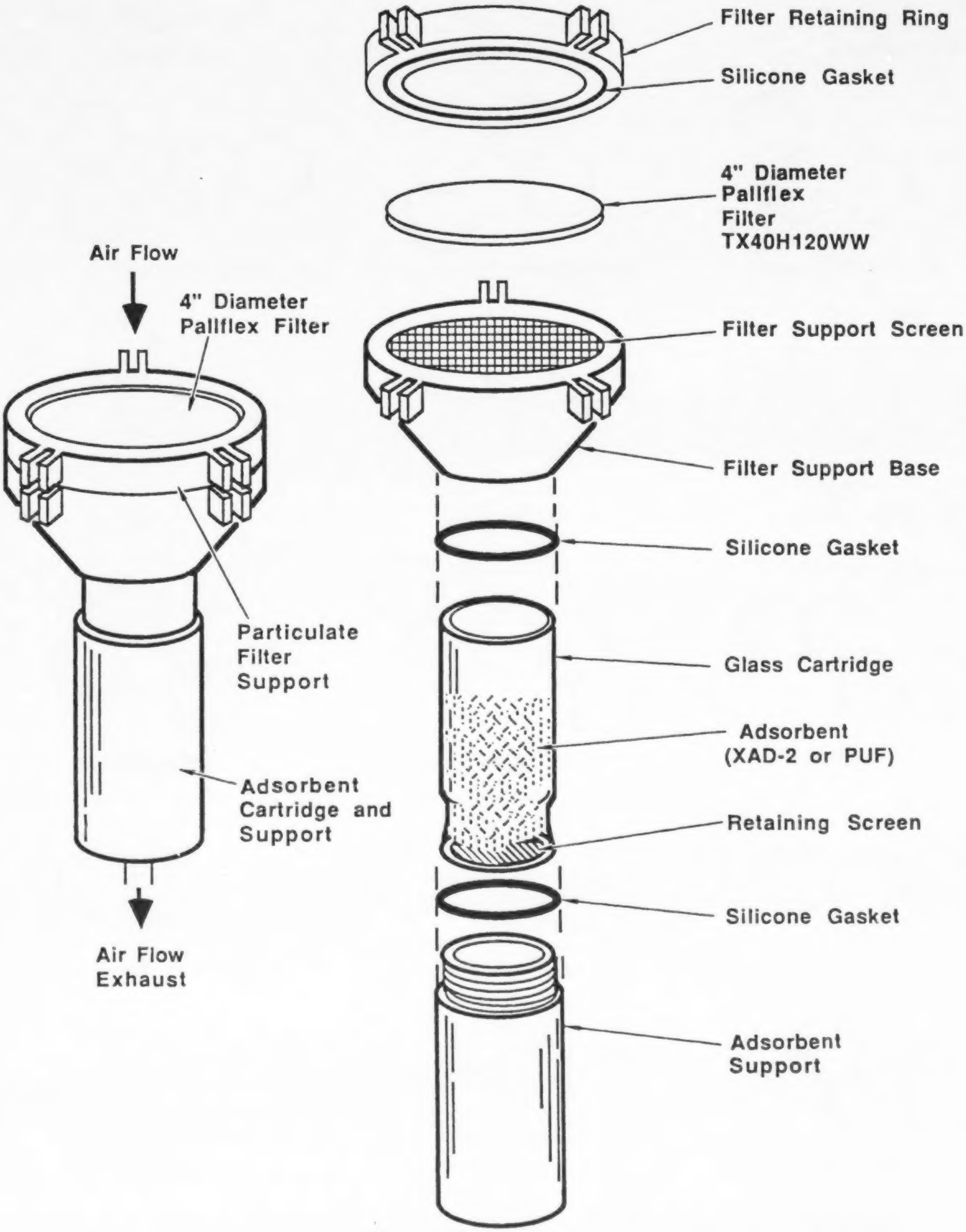
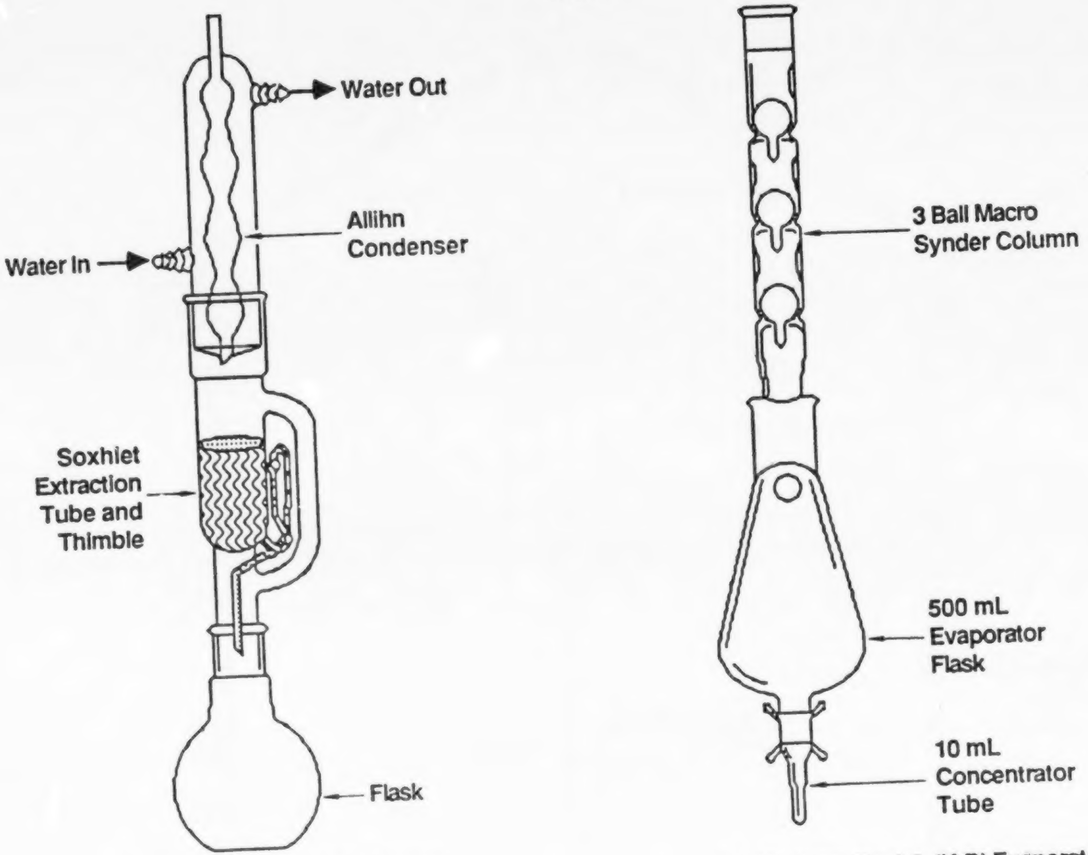
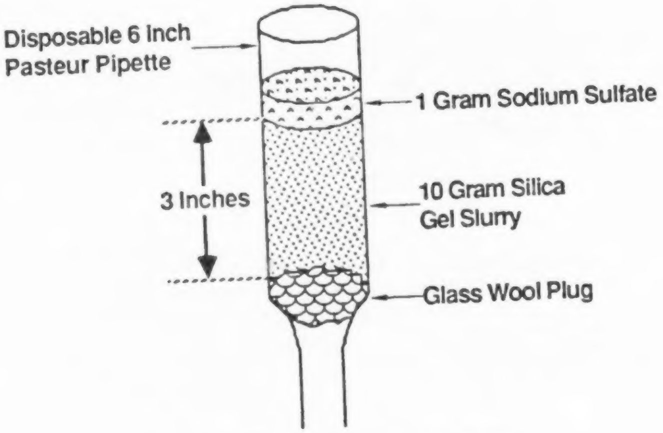

Filter Retaining Ring
Silicone Gasket
4" Diameter Pallflex Filter TX40H120WW
Air Flow
4" Diameter Pallflex Filter
Filter Support Screen
Filter Support Base
Silicone Gasket
Particulate Filter Support
Glass Cartridge
Adsorbent (XAD-2 or PUF)
Adsorbent Cartridge and Support
Retaining Screen
Silicone Gasket
Air Flow Exhaust
Adsorbent Support

FIGURE 2.0 GENERAL METAL WORKS SAMPLING HEAD


Water Out
Allihn Condenser
Water In
Soxhlet Extraction Tube and Thimble
Flask
3 Ball Macro Synder Column
500 mL Evaporator Flask
10 mL Concentrator Tube

(a) Soxhlet Extraction Apparatus with Allihn Condenser

(b) Kuderna-Danish (K-D) Evaporator with Macro Synder Column


Disposable 6 Inch Pasteur Pipette
1 Gram Sodium Sulfate
3 Inches
10 Gram Silica Gel Slurry
Glass Wool Plug

(c) Silica Gel Clean-up Column

FIGURE 3. APPARATUS USES IN SAMPLING ANALYSIS.

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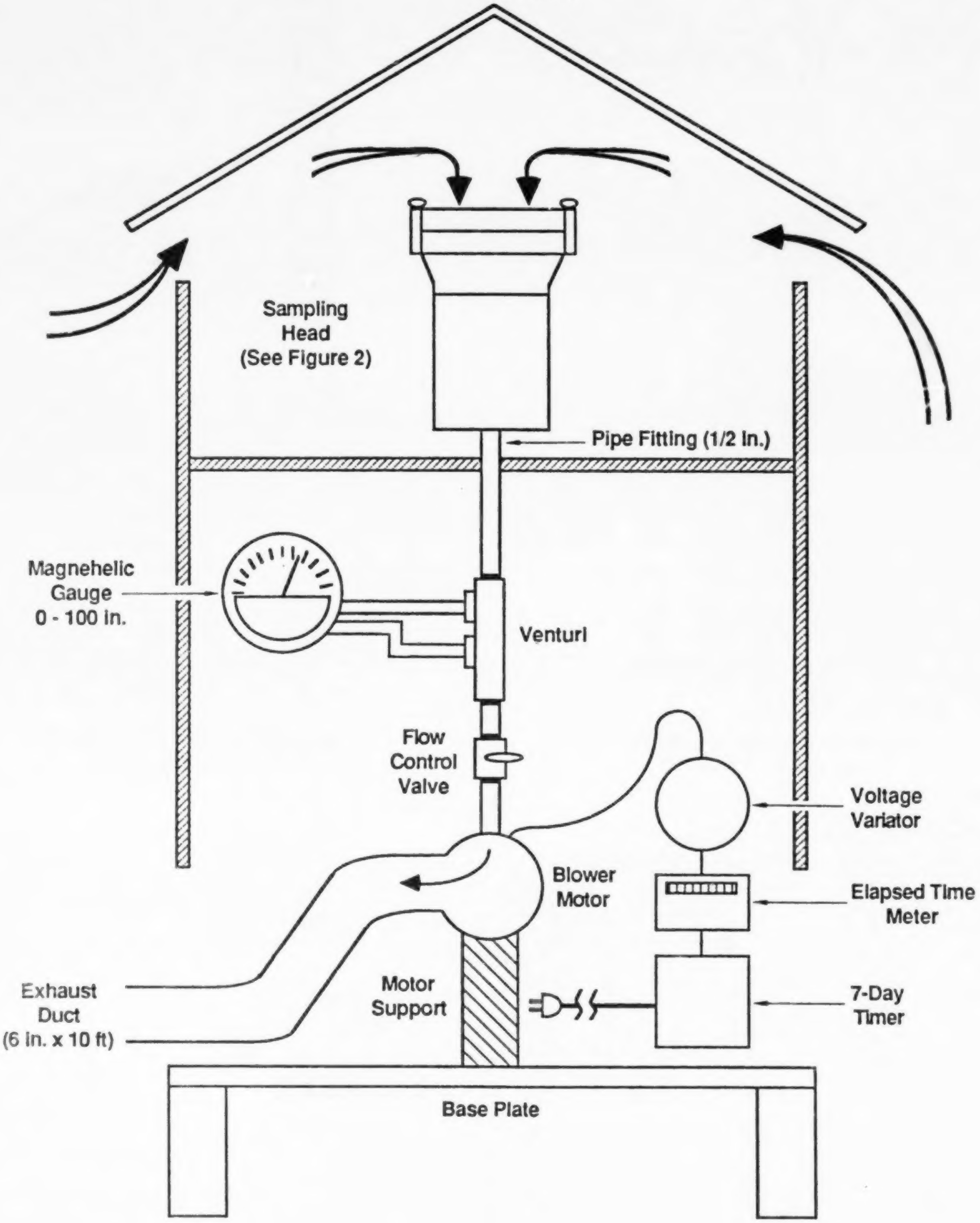
Sampling
Head
(See Figure 2)
Pipe Fitting (1/2 In.)
Magnehelic
Gauge
0 - 100 In.
Venturi
Flow
Control
Valve
Voltage
Variator
Blower
Motor
Elapsed Time
Meter
Exhaust
Duct
(6 In. x 10 ft)
Motor
Support
7-Day
Timer
Base Plate

FIGURE 4. MODIFIED HIGH VOLUME AIR SAMPLER
GENERAL METAL WORKS MODEL PS-1 SAMPLER

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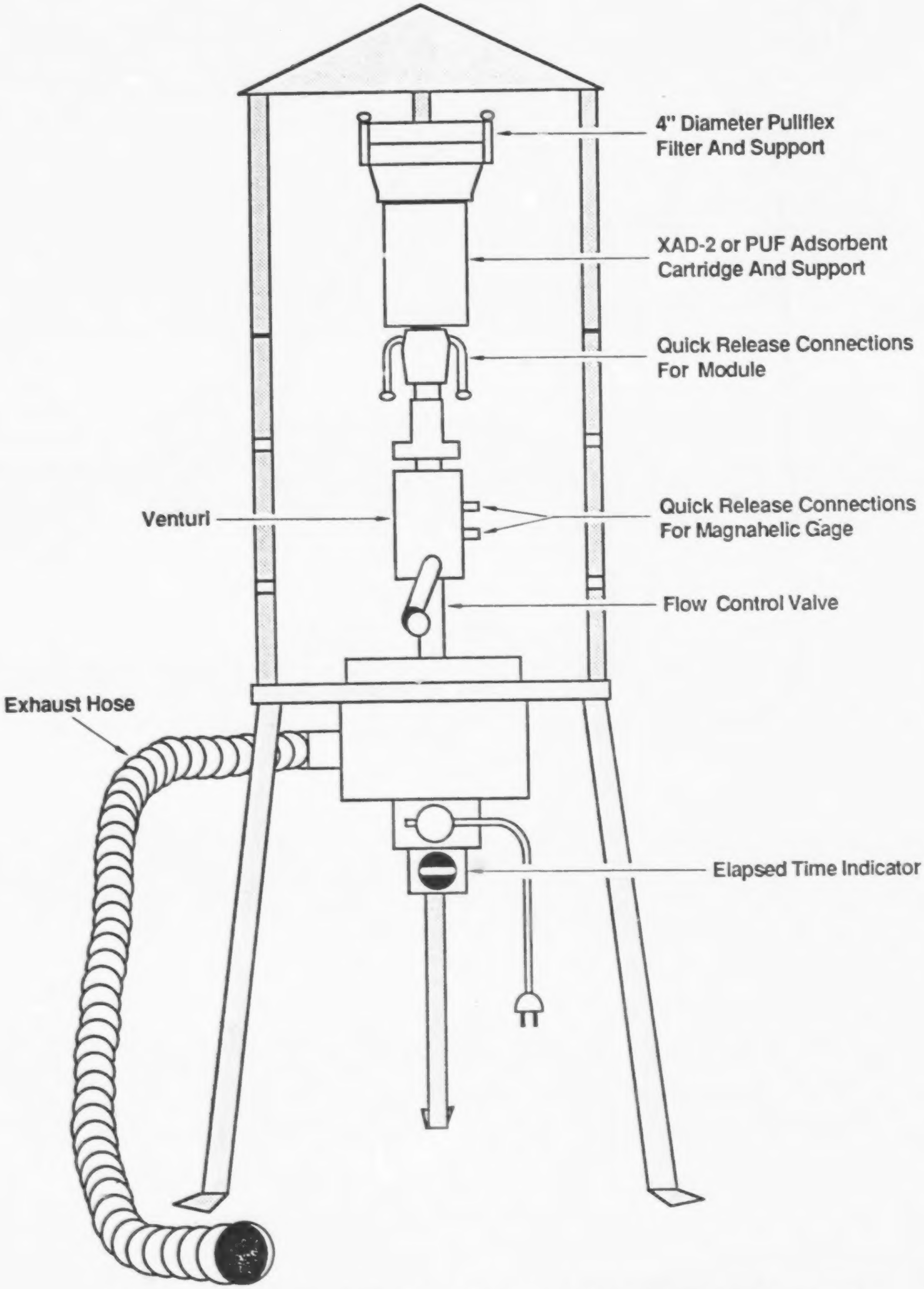
4" Diameter Pullflex
Filter And Support
XAD-2 or PUF Adsorbent
Cartridge And Support
Quick Release Connections
For Module
Venturi
Quick Release Connections
For Magnahelic Gage
Flow Control Valve
Exhaust Hose
Elapsed Time Indicator

FIGURE 5. PORTABLE HIGH VOLUME AIR SAMPLER

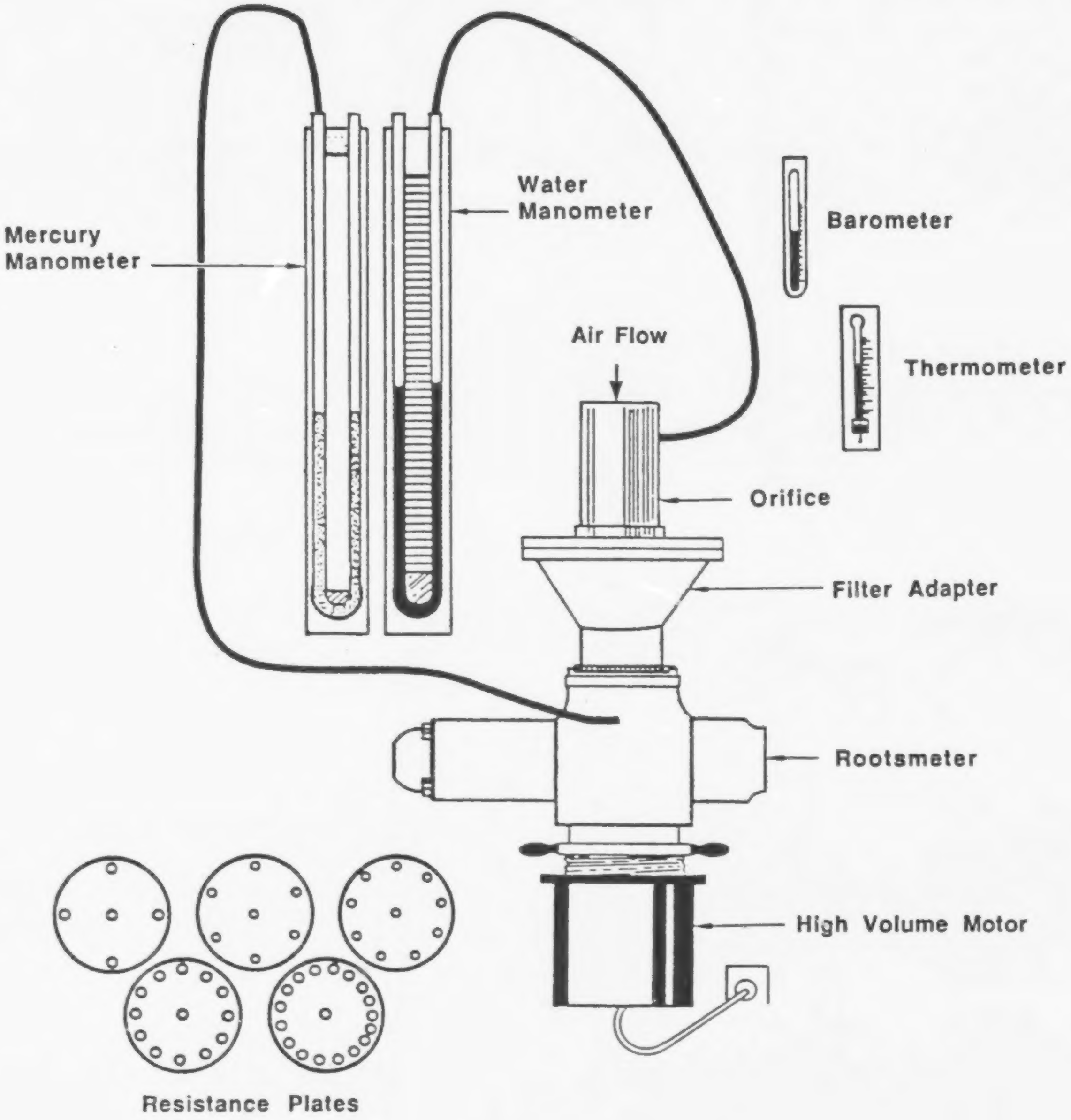
Water
Manometer
Mercury
Manometer
Barometer
Air Flow
Thermometer
Orifice
Filter Adapter
Rootsmeter
High Volume Motor
Resistance Plates

FIGURE 6. LABORATORY ORIFICE CALIBRATION SETUP

T_1 ______________ °C ______________ K

P_1 ______________ mmHg

Orifice No. ______________

Roots Meter No. ______________

Name ______________

Date ______________

Resistance Plates (No. of Holes)	Air Volume Measured By Rootsmeter V_m		Standard Volume V_{std} (std m^3)	Time For Air Volume To Pass Through Rootsmeter Θ (min)	Roots Meter Pressure Differential ΔP (mm Hg)	Pressure Drop Across Orifice ΔH (in. H_2O)	x-Axis Standard Flow Rate Q_{std} (std m^3/min)	y-Axis $\sqrt{\Delta H (P_1 / P_{std})(298 / T_1)}$ Value
	(ft^3)	(m^3)						
5	200	5.66						
7	200	5.66						
10	300	8.50						
13	300	8.50						
18	300	8.50						

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Factors: $(ft^3)\left(0.02832 \frac{m^3}{ft^3}\right) = m^3$ and $(in. Hg)\ 25.4 \left(\frac{mm\ Hg}{in.\ Hg}\right) = mm\ Hg$.

Calculation Equations:

1. $V_{std} = V_m \left(\frac{P_1 - \Delta P}{P_{std}}\right)\left(\frac{T_{std}}{T_1}\right)$ Where: $T_{std} = 298\ K$, $P_{std} = 760.0\ mm\ Hg$

2. $Q_{std} = \frac{V_{std}}{\Theta}$

FIGURE 7. ORIFICE CALIBRATION DATA SHEET.

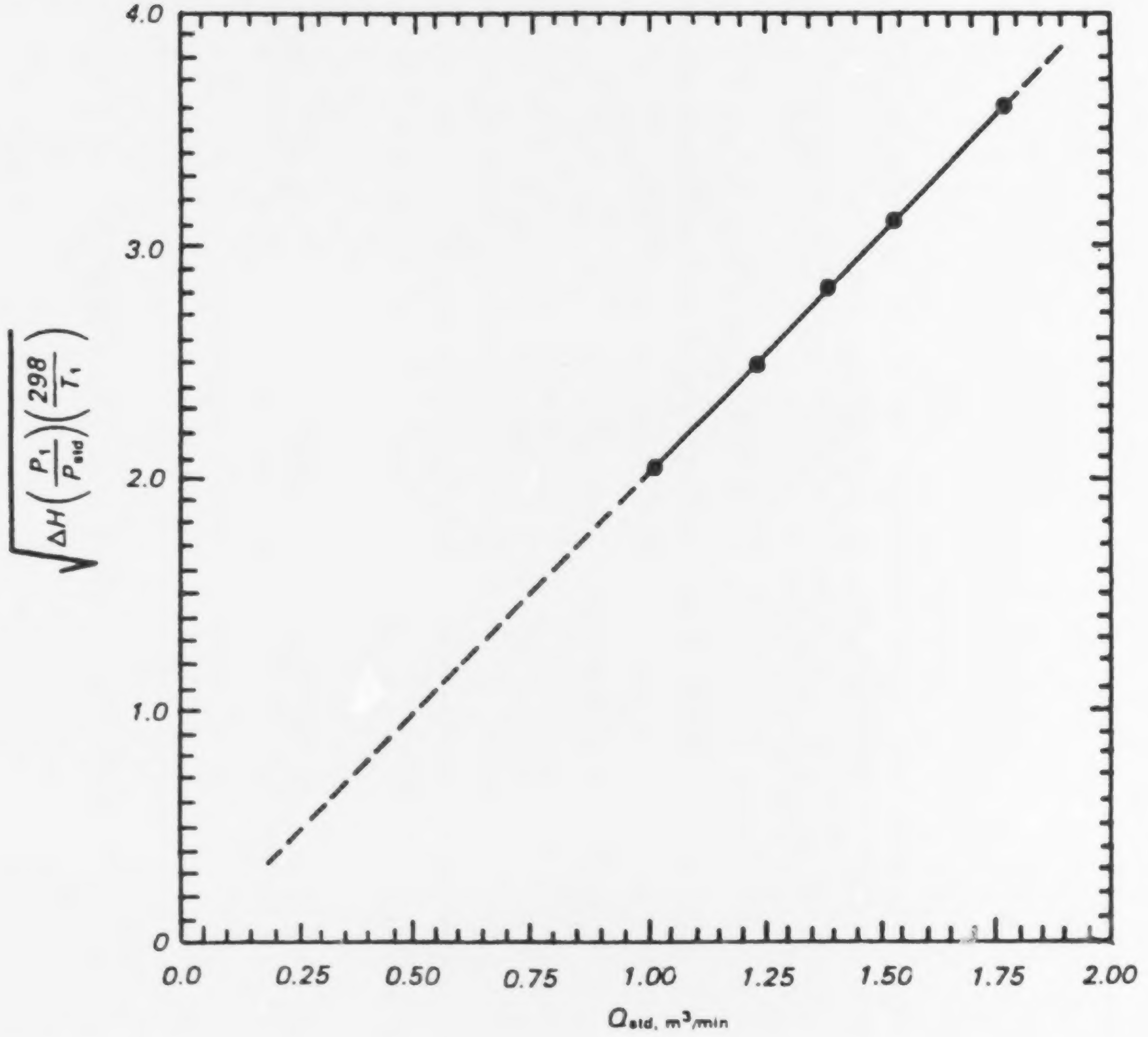

FIGURE 8. ORIFICE METER CALIBRATION CURVE

Performed by ____________ Calibration Orifice ____________ S/N ____________ Ambient Temperature ____________ °C

Date/Time ____________ Manometer S/N ____________ Bar. Press. ____________ mm Hg

Sampler S/N	Variac Setting V	Timer OK? Yes/No	Flow Rate Transfer Standard		Sampler Venturi Date		Comments
			Manometer In. H_2O	Q_{std}[a]	Magnehelic, In. H_2O	Q_{ms}[b]	

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[a] From Calibration Curve For Flow Rate Transfer Standard (Section 11.2.1).

[b] From Calibration Curve for Venturi Tube Using Flow Rate Transfer Standard (Section 11.2.2.9).

FIGURE 9. FIELD CALIBRATION DATA SHEET

Sampler Site ______

Sampler Location ______

Date ______

	Before	After
Barometric Pressure		
Ambient Temperature		

Site ______ Date ______ Performed By ______

Sampler S/N	Sampling Location I.D.	Height Above Ground	Identification No.		Sampling Period		Totaling Sampling Time, min.	Pump Timer Hr. Min.	Sampler Flow Check[1]				
			Filter	XAD-2 or PUF	Start	Stop			Manometer Δ H, Inches of Water	Q_{xs}	M	Q_{ms}	Within ± 10%

[1] Must Be Performed Before and After Each Sampling Period

Checked By ______

Date ______

FIGURE 10. FIELD TEST DATA SHEET.

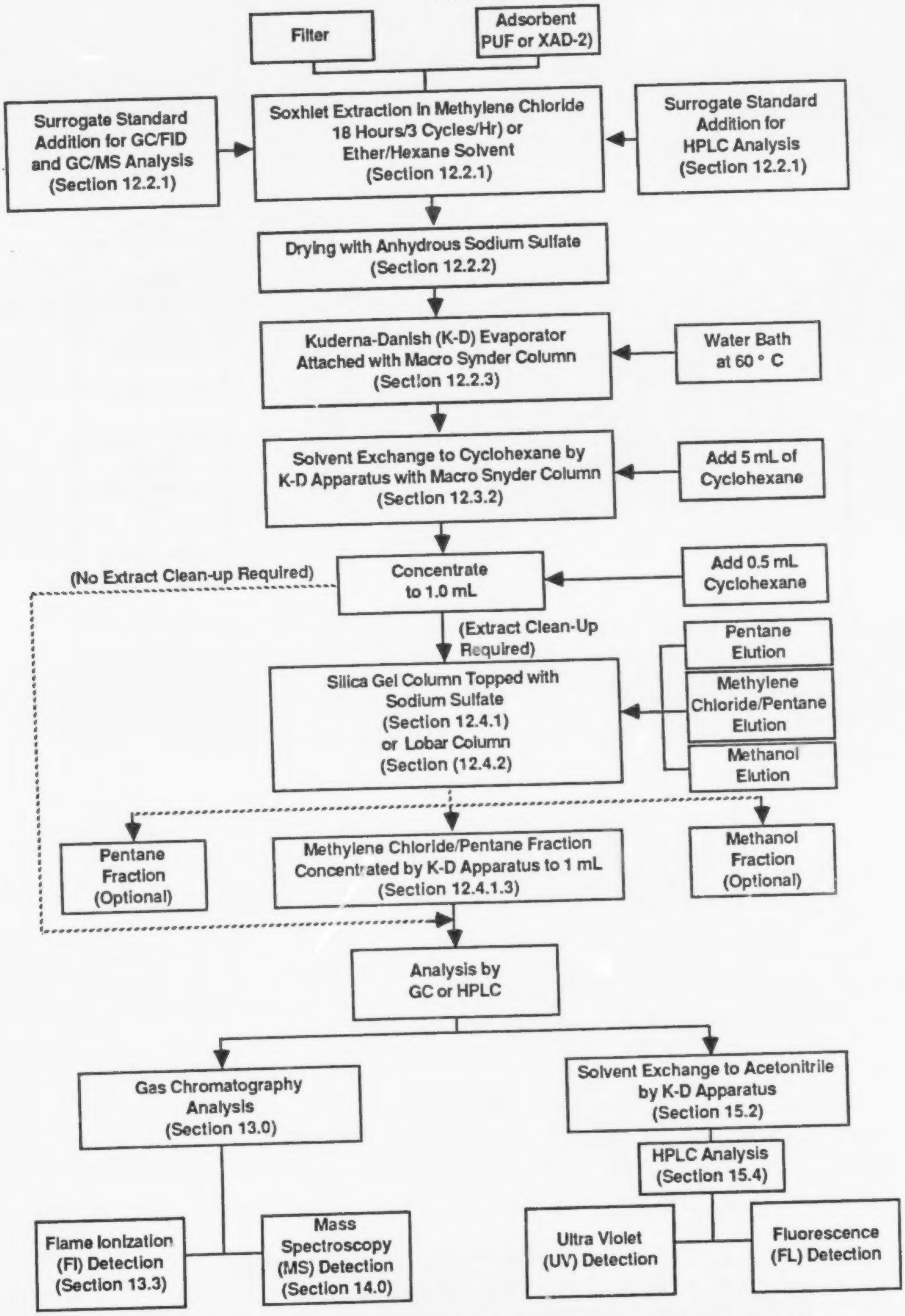

Filter
Adsorbent PUF or XAD-2)
Surrogate Standard Addition for GC/FID and GC/MS Analysis (Section 12.2.1)
Soxhlet Extraction in Methylene Chloride 18 Hours/3 Cycles/Hr) or Ether/Hexane Solvent (Section 12.2.1)
Surrogate Standard Addition for HPLC Analysis (Section 12.2.1)
Drying with Anhydrous Sodium Sulfate (Section 12.2.2)
Kuderna-Danish (K-D) Evaporator Attached with Macro Synder Column (Section 12.2.3)
Water Bath at 60 ° C
Solvent Exchange to Cyclohexane by K-D Apparatus with Macro Snyder Column (Section 12.3.2)
Add 5 mL of Cyclohexane
(No Extract Clean-up Required)
Concentrate to 1.0 mL
Add 0.5 mL Cyclohexane
(Extract Clean-Up Required)
Pentane Elution
Silica Gel Column Topped with Sodium Sulfate (Section 12.4.1) or Lobar Column (Section (12.4.2)
Methylene Chloride/Pentane Elution
Methanol Elution
Pentane Fraction (Optional)
Methylene Chloride/Pentane Fraction Concentrated by K-D Apparatus to 1 mL (Section 12.4.1.3)
Methanol Fraction (Optional)
Analysis by GC or HPLC
Gas Chromatography Analysis (Section 13.0)
Solvent Exchange to Acetonitrile by K-D Apparatus (Section 15.2)
HPLC Analysis (Section 15.4)
Flame Ionization (FI) Detection (Section 13.3)
Mass Spectroscopy (MS) Detection (Section 14.0)
Ultra Violet (UV) Detection
Fluorescence (FL) Detection

FIGURE 11.0. SAMPLE CLEAN-UP, CONCENTRATION, SEPARATION AND ANALYSIS SEQUENCE.

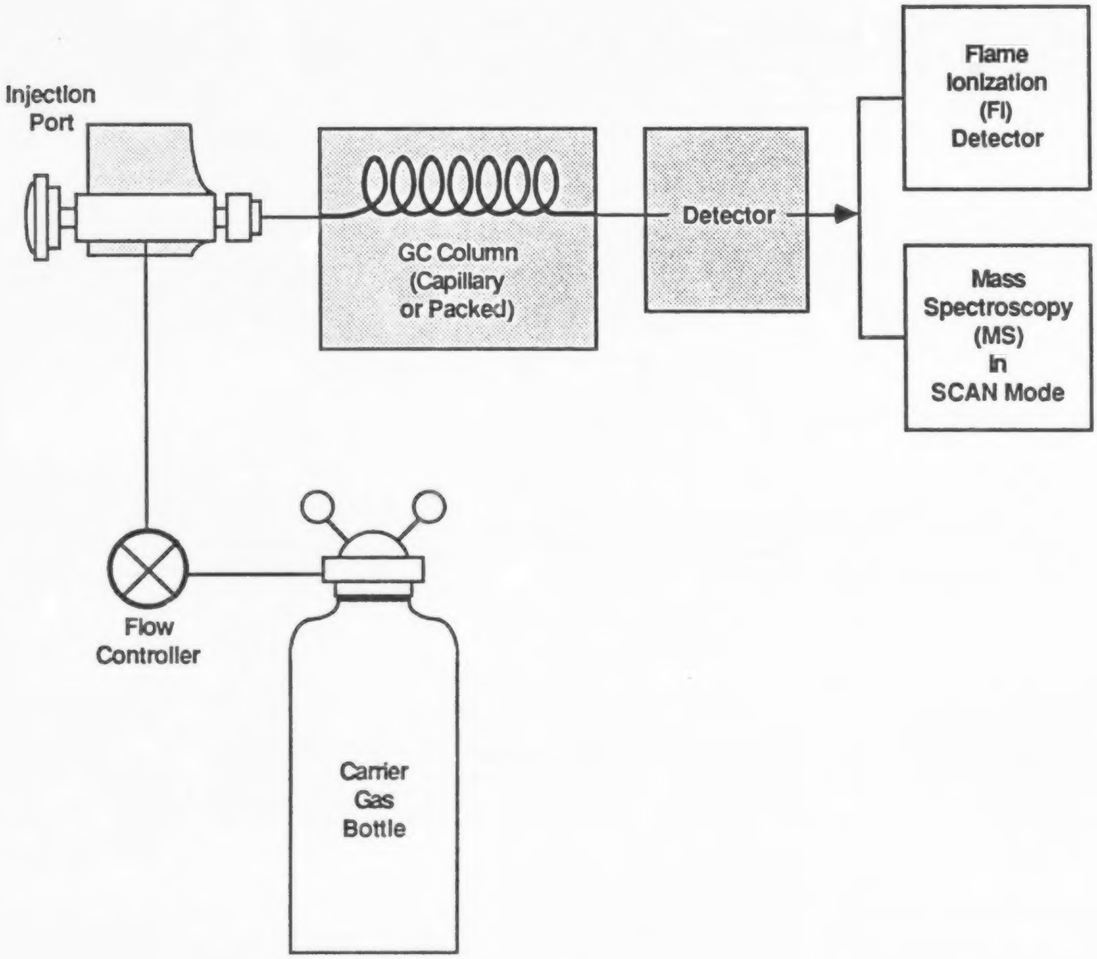

Injection Port
GC Column (Capillary or Packed)
Detector
Flame Ionization (FI) Detector
Mass Spectroscopy (MS) In SCAN Mode
Flow Controller
Carrier Gas Bottle

FIGURE 12.0 GC SEPARATION WITH SUBSEQUENT FLAME IONIZATION (FI) OR MASS SPECTROSCOPY (MS) DETECTION.

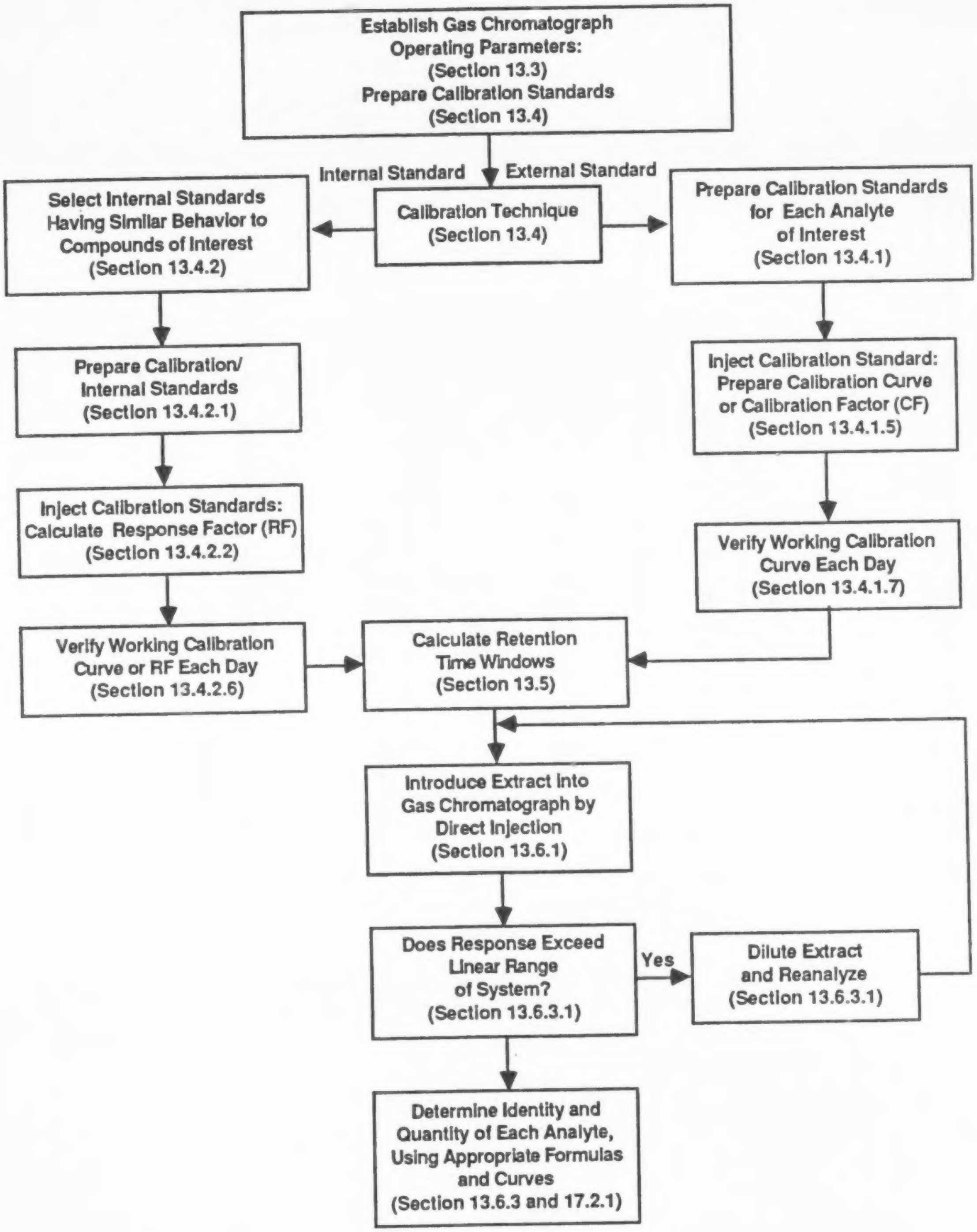
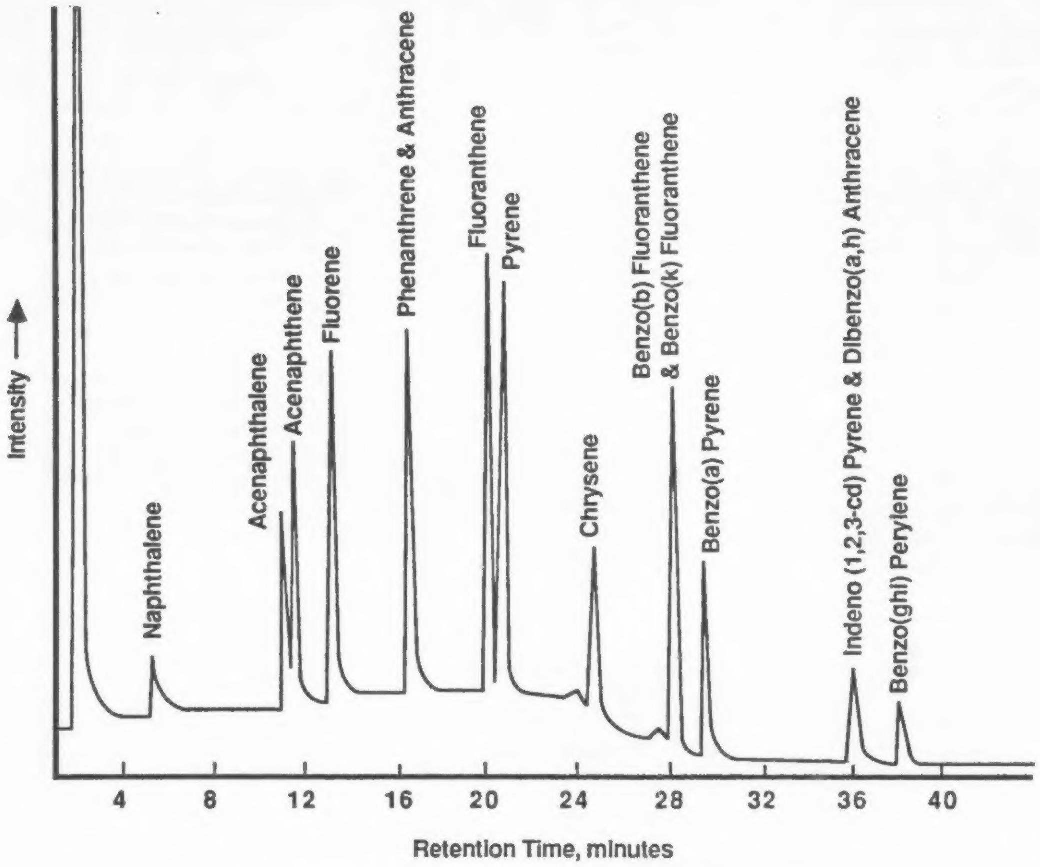

Establish Gas Chromatograph Operating Parameters: (Section 13.3) Prepare Calibration Standards (Section 13.4)
Internal Standard
External Standard
Calibration Technique (Section 13.4)
Select Internal Standards Having Similar Behavior to Compounds of Interest (Section 13.4.2)
Prepare Calibration Standards for Each Analyte of Interest (Section 13.4.1)
Prepare Calibration/ Internal Standards (Section 13.4.2.1)
Inject Calibration Standard: Prepare Calibration Curve or Calibration Factor (CF) (Section 13.4.1.5)
Inject Calibration Standards: Calculate Response Factor (RF) (Section 13.4.2.2)
Verify Working Calibration Curve Each Day (Section 13.4.1.7)
Verify Working Calibration Curve or RF Each Day (Section 13.4.2.6)
Calculate Retention Time Windows (Section 13.5)
Introduce Extract into Gas Chromatograph by Direct Injection (Section 13.6.1)
Does Response Exceed Linear Range of System? (Section 13.6.3.1)
Yes
Dilute Extract and Reanalyze (Section 13.6.3.1)
Determine Identity and Quantity of Each Analyte, Using Appropriate Formulas and Curves (Section 13.6.3 and 17.2.1)

FIGURE 13.0 GC CALIBRATION AND RETENTION TIME WINDOW DETERMINATION.



Column: 3% OV-17 on Chromosorb W-AW-DCMS
Program: 100 °C. 4 min., 8 ° per min. to 280 °C.
Detector: Flame Ionization

FIGURE 14.0 TYPICAL CHROMATOGRAM OF SELECTIVE PNAs BY GC EQUIPPED WITH FI DETECTOR.

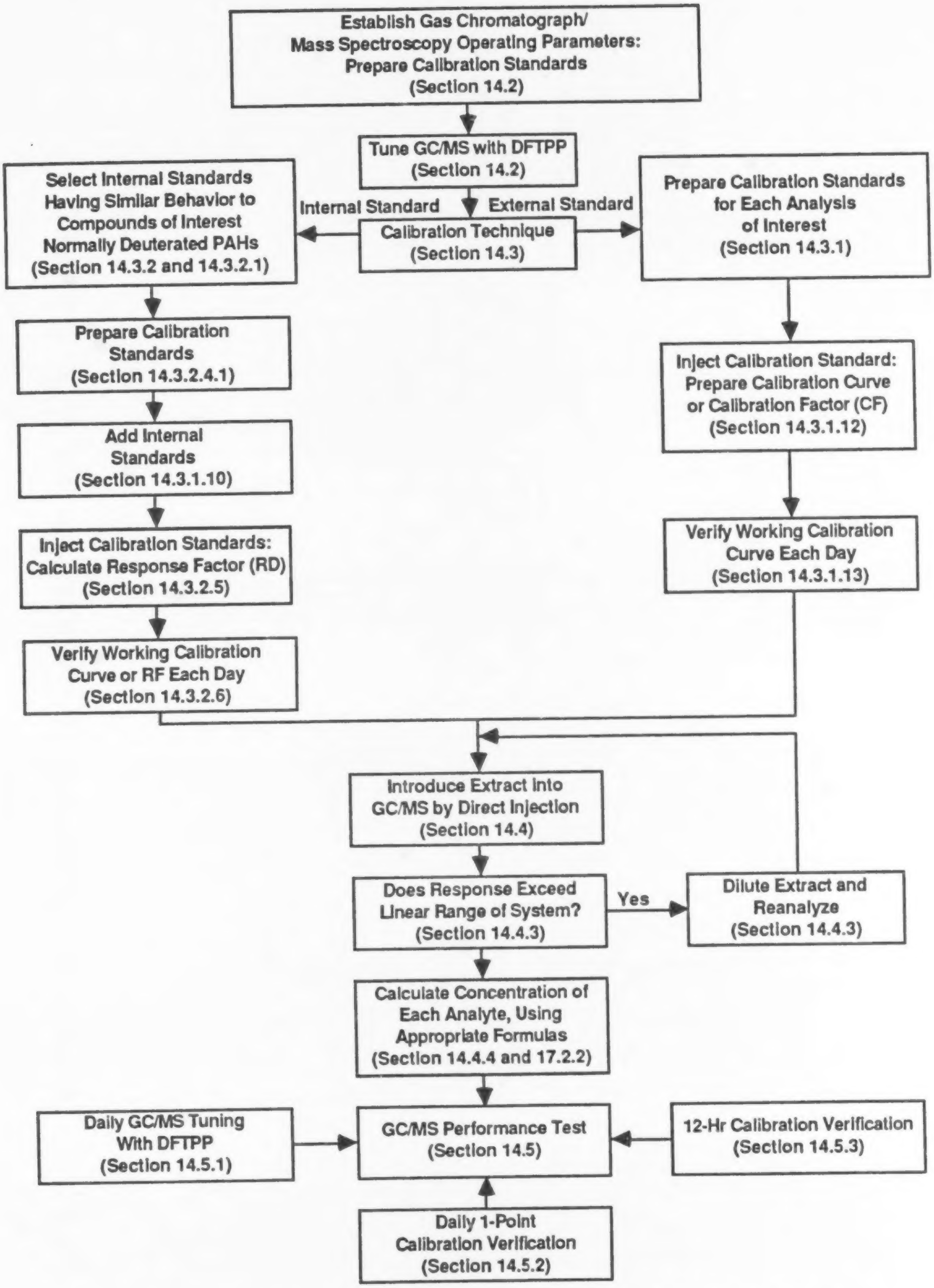

Establish Gas Chromatograph/ Mass Spectroscopy Operating Parameters: Prepare Calibration Standards (Section 14.2)
Tune GC/MS with DFTPP (Section 14.2)
Internal Standard
External Standard
Calibration Technique (Section 14.3)
Select Internal Standards Having Similar Behavior to Compounds of Interest Normally Deuterated PAHs (Section 14.3.2 and 14.3.2.1)
Prepare Calibration Standards for Each Analysis of Interest (Section 14.3.1)
Prepare Calibration Standards (Section 14.3.2.4.1)
Add Internal Standards (Section 14.3.1.10)
Inject Calibration Standards: Calculate Response Factor (RD) (Section 14.3.2.5)
Verify Working Calibration Curve or RF Each Day (Section 14.3.2.6)
Inject Calibration Standard: Prepare Calibration Curve or Calibration Factor (CF) (Section 14.3.1.12)
Verify Working Calibration Curve Each Day (Section 14.3.1.13)
Introduce Extract into GC/MS by Direct Injection (Section 14.4)
Does Response Exceed Linear Range of System? (Section 14.4.3)
Yes
Dilute Extract and Reanalyze (Section 14.4.3)
Calculate Concentration of Each Analyte, Using Appropriate Formulas (Section 14.4.4 and 17.2.2)
Daily GC/MS Tuning With DFTPP (Section 14.5.1)
GC/MS Performance Test (Section 14.5)
12-Hr Calibration Verification (Section 14.5.3)
Daily 1-Point Calibration Verification (Section 14.5.2)

FIGURE 15.0 GC/MS CALIBRATION AND ANALYSIS.

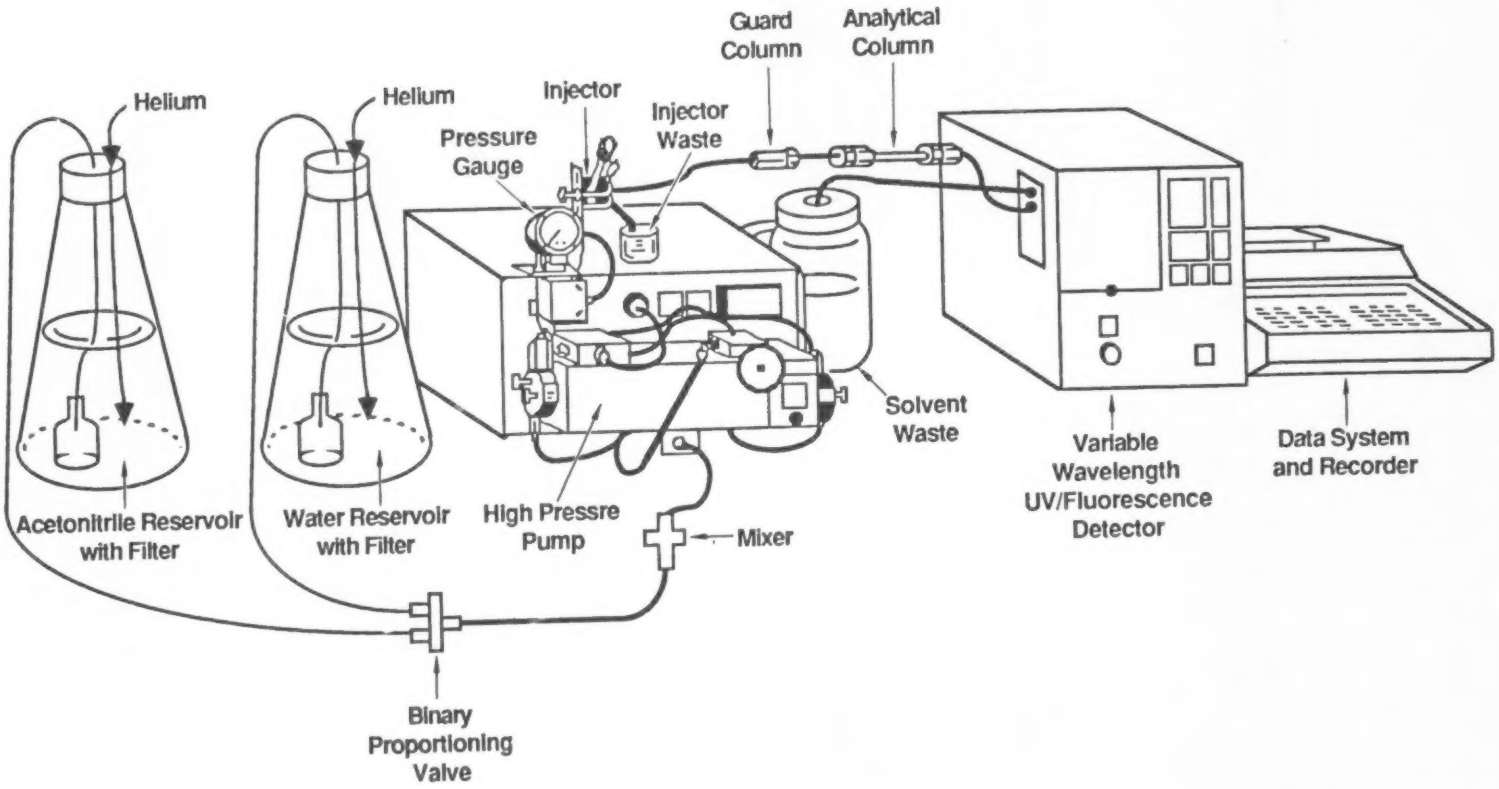

Helium
Helium
Injector
Pressure Gauge
Injector Waste
Guard Column
Analytical Column
Acetonitrile Reservoir with Filter
Water Reservoir with Filter
High Pressre Pump
Mixer
Solvent Waste
Variable Wavelength UV/Fluorescence Detector
Data System and Recorder
Binary Proportioning Valve

FIGURE 16. IMPORTANT COMPONENTS OF AN HPLC SYSTEM.

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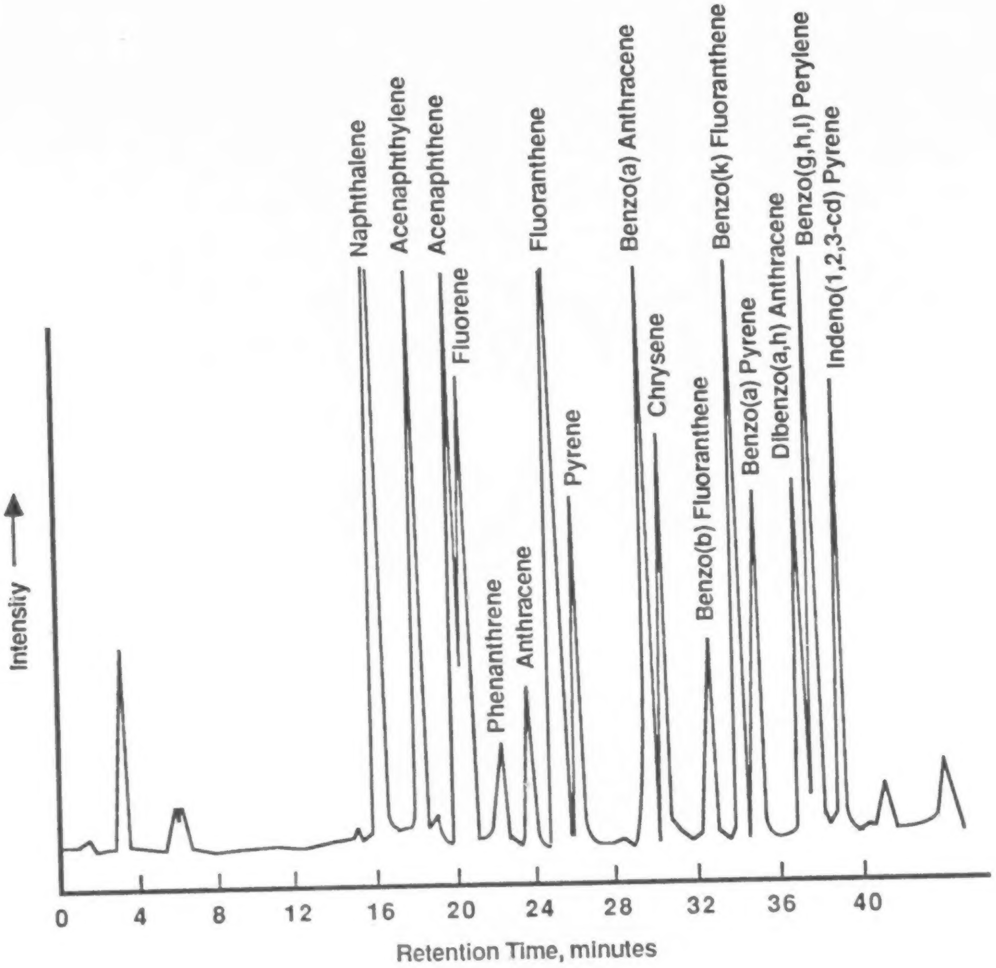

FIGURE 17.0 TYPICAL CHROMATOGRAM OF SELECTIVE PAHs ASSOCIATES WITH HPLC ANALYSIS WITH FLUORESCENCE DETECTION.

METHOD TO14 -/

DETERMINATION OF VOLATILE ORGANIC COMPOUNDS (VOCs) IN AMBIENT AIR USING SUMMA® PASSIVATED CANISTER SAMPLING AND GAS CHROMATOGRAPHIC ANALYSIS

1. Scope

1.1 This document describes a procedure for sampling and analysis of volatile organic compounds (VOCs) in ambient air. The method is based on collection of whole air samples in SUMMA® passivated stainless steel canisters. The VOCs are subsequently separated by gas chromatography and measured by mass-selective detector or multidetector techniques. This method presents procedures for sampling into canisters to final pressures both above and below atmospheric pressure (respectively referred to as pressurized and subatmospheric pressure sampling).

1.2 This method is applicable to specific VOCs that have been tested and determined to be stable when stored in pressurized and subatmospheric pressure canisters. Numerous compounds, many of which are chlorinated VOCs, have been successfully tested for storage stability in pressurized canisters (1,2). However, minimal documentation is currently available demonstrating stability of VOCs in subatmospheric pressure canisters.

1.3 The organic compounds that have been successfully collected in pressurized canisters by this method are listed in Table 1. These compounds have been successfully measured at the parts per billion by volume (ppbv) level.

2. Applicable Documents

2.1 ASTM Standards

D1356 - Definition of Terms Related to Atmospheric Sampling and Analysis
E260 - Recommended Practice for General Gas Chromatography Procedures
E355 - Practice for Gas Chromatography Terms and Relationships

2.2 Other Documents

U.S. Environmental Protection Agency Technical Assistance Document (3)

Laboratory and Ambient Air Studies (4-17)

METHOD TO14 -2

DETERMINATION OF VOLATILE ORGANIC COMPOUNDS (VOCs) IN AMBIENT AIR USING SUMMA® PASSIVATED CANISTER SAMPLING AND GAS CHROMATOGRAPHIC ANALYSIS

OUTLINE

1. Scope
2. Applicable Documents
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4. Significance
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6. Interferences and Limitations
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        7.1.2 Pressurized
    7.2 Sample Analysis
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        7.2.2 GC-MS-SIM Analytical System
        7.2.3 GC-Multidetector Analytical System
    7.3 Canister Cleaning System
    7.4 Calibration System and Manifold
8. Reagents and Materials
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    9.1 System Description
        9.1.1 Subatmospheric Pressure Sampling
        9.1.2 Pressurized Sampling
        9.1.3 All Samplers
    9.2 Sampling Procedure
10. Analytical System
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        10.1.3 GC-Multidetector (GC-FID-ECD-PID) System
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        10.2.1 GC-MS System Operation
        10.2.2 Daily GC-MS Tuning
        10.2.3 GC-MS Calibration
            10.2.3.1 Initial Calibration
            10.2.3.2 Routine Calibration
    10.3 GC-FID-ECD System Performance Criteria (With Optional PID)
        10.3.1 Humid Zero Air Certification
        10.3.2 GC Retention Time Windows Determination
        10.3.3 GC Calibration
            10.3.3.1 Initial Calibration
            10.3.3.2 Routine Calibration
        10.3.4 GC-FID-ECD-PID System Performance Criteria
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        10.4.3 GC-MS-SIM Analysis (With Optional FID System)
        10.4.4 GC-FID-ECD Analysis (With Optional PID System)

OUTLINE (Cont.)

11. Cleaning and Certification Program
    - 11.1 Canister Cleaning and Certification
    - 11.2 Sampling System Cleaning and Certification
        - 11.2.1 Cleaning Sampling System Components
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12. Performance Criteria and Quality Assurance
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        - 12.3.2 Analysis
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    - 12.5 Quality Assurance
        - 12.5.1 Sampling System
        - 12.5.2 GC-MS-SCAN-SIM System Performance Criteria
        - 12.5.3 GC-Multidetector System Performance Criteria

13. Acknowledgements

14. References

APPENDIX A - Availability of Audit Cylinders from U.S. Environmental Protection Agency (USEPA) to USEPA Program/Regional Offices, State/Local Agencies and Their Contractors

APPENDIX B - Operating Procedures for a Portable Gas Chromatograph Equipped With a Photoionization Detector

APPENDIX C - Installation and Operating Procedures for Alternative Air Toxics Samplers

3. Summary of Method

3.1 Both subatmospheric pressure and pressurized sampling modes use an initially evacuated canister and a pump-ventilated sample line during sample collection. Pressurized sampling requires an additional pump to provide positive pressure to the sample canister. A sample of ambient air is drawn through a sampling train comprised of components that regulate the rate and duration of sampling into a pre-evacuated SUMMA® passivated canister.

3.2 After the air sample is collected, the canister valve is closed, an identification tag is attached to the canister, and the canister is transported to a predetermined laboratory for analysis.

3.3 Upon receipt at the laboratory, the canister tag data is recorded and the canister is attached to the analytical system. During analysis, water vapor is reduced in the gas stream by a Nafion® dryer (if applicable), and the VOCs are then concentrated by collection in a cryogenically-cooled trap. The cryogen is then removed and the temperature of the trap is raised. The VOCs originally collected in the trap are revolatilized, separated on a GC column, then detected by one or more detectors for identification and quantitation.

3.4 The analytical strategy for Method TO14 involves using a high-resolution gas chromatograph (GC) coupled to one or more appropriate GC detectors. Historically, detectors for a GC have been divided into two groups: non-specific detectors and specific detectors. The non-specific detectors include, but are not limited to, the nitrogen-phosphorus detector (NPD), the flame ionization detector (FID), the electron capture detector (ECD) and the photoionization detector (PID). The specific detectors include the mass spectrometer (MS) operating in either the selected ion monitoring (SIM) mode or the SCAN mode, or the ion trap detector. The use of these detectors or a combination of these detectors as part of an analytical scheme is determined by the required specificity and sensitivity of the application. While the non-specific detectors are less expensive per analysis and in some cases more sensitive than the specific detector, they vary in specificity and sensitivity for a specific class of compounds. For instance, if multiple halogenated compounds are targeted, an ECD is usually chosen; if only compounds containing nitrogen or phosphorus are of interest, a NPD can be used; or, if a variety of hydrocarbon compounds are sought, the broad response of the FID or PID is appropriate. In each of these cases, however, the specific identification of the compound within the class is determined only by its retention time, which can be subject to shifts or to interference from other nontargeted compounds. When misidentification occurs, the error is generally a result of a cluttered chromatogram, making peak assignment difficult. In particular, the more volatile organics (chloroethanes, ethyltoluenes, dichlorobenzenes, and various freons) exhibit less well defined chromatographic peaks, leading to misidentification using non-specific detectors. Quantitative comparisons indicate that the FID is more subject to error than the ECD because the ECD is a much more selective detector for a smaller class of compounds which exhibits a stronger response. Identification errors, however, can be reduced by: (a) employing simultaneous detection by different detectors or (b) correlating retention times from different GC columns for confirmation. In either case, interferences on the non-specific detectors can still cause error in identifying a complex sample. The non-specific detector system (GC-NPD-FID-ECD-PID), however, has been used for approximate quantitation of relatively clean samples. The nonspecific detector system can provide a "snapshot" of the constituents in the sample, allowing determination of:

- Extent of misidentification due to overlapping peaks,
- Position of the VOCs within or not within the concentration range of anticipated further analysis by specific detectors (GC-MS-SCAN-SIM) (if not, the sample is further diluted), and
- Existence of unexpected peaks which need further identification by specific detectors.

On the other hand, the use of specific detectors (MS coupled to a GC) allows positive compound identification, thus lending itself to more specificity than the multidetector GC. Operating in the SIM mode, the MS can readily approach the same sensitivity as the multidetector system, but its flexibility is limited. For SIM operation, the MS is programmed to acquire data for a limited number of targeted compounds while disregarding other acquired information. In the SCAN mode, however, the MS becomes a universal detector, often detecting compounds which are not detected by the multidetector approach. The GC-MS-SCAN will provide positive identification, while the GC-MS-SIM procedure provides quantitation of a restricted "target compound" list of VOCs.

The analyst often must decide whether to use specific or non-specific detectors by considering such factors as project objectives, desired detection limits, equipment availability, cost and personnel capability in developing an analytical strategy.

A list of some of the advantages and disadvantages associated with non-specific and specific detectors may assist the analyst in the decision-making process.

Non-Specific Multidetector Analytical System

Advantages

- o Somewhat lower equipment cost than GC-MS
- o Less sample volume required for analysis
- o More sensitive
    - ECD may be 1000 times more sensitive than GC-MS

Disadvantages

- o Multiple detectors to calibrate
- o Compound identification not positive
- o Lengthy data interpretation (one hour each for analysis and data reduction)
- o Interference(s) from co-eluting compound(s)
- o Cannot identify unknown compounds
    - outside range of calibration
    - without standards
- o Does not differentiate targeted compounds from interfering compounds

Specific Detector Analytical System

GC-MS-SIM

Advantages	Disadvantages
positive compound identification	can't identify non-specified compounds (ions)
greater sensitivity than GC-MS-SCAN	somewhat greater equipment cost than multidetector GC
less operator interpretation than for multidetector GC	greater sample volume required than for multidetector GC
can resolve co-eluting peaks	universality of detector sacrificed to achieve enhancement in sensitivity
more specific than the multidetector GC	

GC-MS-SCAN

positive compound identification	lower sensitivity than GC-MS-SIM
can identify all compounds	greater sample volume required than for multidetector GC
less operator interpretation	somewhat greater equipment cost than multidetector GC
can resolve co-eluting peaks	

The analytical finish for the measurement chosen by the analyst should provide a definitive identification and a precise quantitation of volatile organics. In a large part, the actual approach to these two objectives is subject to equipment availability. Figure 1 indicates some of the favorite options that are used as an analytical finish. The GC-MS-SCAN option uses a capillary column GC coupled to a MS operated in a scanning mode and supported by spectral library search routines. This option offers the nearest approximation to unambiguous identification and covers a wide range of compounds as defined by the completeness of the spectral library. GC-MS-SIM mode is limited to a set of target compounds which are user defined and is more sensitive than GC-MS-SCAN by virtue of the longer dwell times at the restricted number of m/z values. Both these techniques, but especially the GC-MS-SIM option, can use a supplemental general non-specific detector to verify/identify the presence of VOCs. Finally, the option labelled GC-multidetector system uses a combination of retention time and multiple general detector verification to identify compounds. However, interference due to nearly identical retention times can affect system quantitation when using this option.

Due to the low concentrations of VOCs encountered in urban air (typically less than 4 ppbv and the majority below 1 ppbv) along with their complicated chromatograms, Method TO-14 strongly recommends the specific detectors (GC-MS-SCAN-SIM) for positive identification and for primary quantitation to ensure that high-quality ambient data is acquired.

For the experienced analyst whose analytical system is limited to the non-specific detectors, Section 10.3 does provide guidelines and example chromatograms showing typical retention times and calibration response factors, and utilizing the non-specific detectors (GC-FID-ECD-PID) analytical system as the primary quantitative technique.

4. Significance

4.1 VOCs enter the atmosphere from a variety of sources, including petroleum refineries, synthetic organic chemical plants, natural gas processing plants, and automobile exhaust. Many of these VOCs are acutely toxic; therefore, their determination in ambient air is necessary to assess human health impacts.

4.2 Conventional methods for VOC determination use solid sorbent sampling techniques. The most widely used solid sorbent is Tenax®. An air sample is drawn through a Tenax®-filled cartridge where certain VOCs are trapped on the polymer. The sample cartridge is transferred to a laboratory and analyzed by GC-MS.

4.3 VOCs can also be successfully collected in stainless steel canisters. Collection of ambient air samples in canisters provides (1) convenient integration of ambient samples over a specific time period, (e.g., 24 hours); (2) remote sampling and central analysis; (3) ease of storing and shipping samples; (4) unattended sample collection; (5) analysis of samples from multiple sites with one analytical system; and (6) collection of sufficient sample volume to allow assessment of measurement precision and/or analysis of samples by several analytical systems. However, care must be exercised in selecting, cleaning, and handling sample canisters and sampling apparatus to avoid losses or contamination of the samples. Contamination is a critical issue with canister-based sampling because the canister is the last element in the sampling train.

4.4 Interior surfaces of the canisters are treated by the SUMMA® passivation process, in which a pure chrome-nickel oxide is formed on the surface. This type of vessel has been used in the past for sample collection and has demonstrated sample storage stability of many specific organic compounds.

4.5 This method can be applied to sampling and analysis of not only VOCs, but also some selected semivolatile organic compounds (SVOCs). The term "semivolatile organic compounds" is used to broadly describe organic compounds that are too volatile to be collected by filtration air sampling but not volatile enough for thermal desorption from solid sorbents. SVOCs can generally be classified as those with saturation vapor pressures at 25°C between 10^{-1} and 10^{-7} mm Hg. VOCs are generally classified as those organics having saturated vapor pressures at 25°C greater than 10^{-1} mm Hg.

5. Definitions

Note: Definitions used in this document and in any user-prepared Standard Operating Procedures (SOPs) should be consistent with ASTM Methods D1356, E260, and E355. All abbreviations and symbols within this method are defined at point of use.

5.1 Absolute canister pressure = Pg+Pa, where Pg = gauge pressure in the canister (kPa, psi) and Pa = barometric pressure (see 5.2).

5.2 Absolute pressure - Pressure measured with reference to absolute zero pressure (as opposed to atmospheric pressure), usually expressed as kPa, mm Hg or psia.

5.3 Cryogen - A refrigerant used to obtain very low temperatures in the cryogenic trap of the analytical system. A typical cryogen is liquid oxygen (bp -183.0°C) or liquid argon (bp -185.7°C).

5.4 Dynamic calibration - Calibration of an analytical system using calibration gas standard concentrations in a form identical or very similar to the samples to be analyzed and by introducing such standards into the inlet of the sampling or analytical system in a manner very similar to the normal sampling or analytical process.

5.5 Gauge pressure - Pressure measured above ambient atmospheric pressure (as opposed to absolute pressure). Zero gauge pressure is equal to ambient atmospheric (barometric) pressure.

5.6 MS-SCAN - The GC is coupled to a MS programmed in the SCAN mode to scan all ions repeatedly during the GC run. As used in the current context, this procedure serves as a qualitative identification and characterization of the sample.

5.7 MS-SIM - The GC is coupled to a MS programmed to acquire data for only specified ions and to disregard all others. This is performed using SIM coupled to retention time discriminators. The GC-SIM analysis provides quantitative results for selected constituents of the sample gas as programmed by the user.

5.8 Megabore® column - Chromatographic column having an internal diameter (I.D.) greater than 0.50 mm. The Megabore® column is a trademark of the J&W Scientific Co. For purposes of this method, Megabore® refers to chromatographic columns with 0.53 mm I.D.

5.9 Pressurized sampling - Collection of an air sample in a canister with a (final) canister pressure above atmospheric pressure, using a sample pump.

5.10 Qualitative accuracy - The ability of an analytical system to correctly identify compounds.

5.11 Quantitative accuracy - The ability of an analytical system to correctly measure the concentration of an identified compound.

5.12 Static calibration - Calibration of an analytical system using standards in a form different than the samples to be analyzed. An example of a static calibration would be injecting a small volume of a high concentration standard directly onto a GC column, bypassing the sample extraction and preconcentration portion of the analytical system.

5.13 Subatmospheric sampling - Collection of an air sample in an evacuated canister at a (final) canister pressure below atmospheric pressure, without the assistance of a sampling pump. The canister is filled as the internal canister pressure increases to ambient or near ambient pressure. An auxiliary vacuum pump may be used as part of the sampling system to flush the inlet tubing prior to or during sample collection.

6. Interferences and Limitations

6.1 Interferences can occur in sample analysis if moisture accumulates in the dryer (see Section 10.1.1.2). An automated cleanup procedure that periodically heats the dryer to about 100°C while purging with zero air eliminates any moisture buildup. This procedure does not degrade sample integrity.

6.2 Contamination may occur in the sampling system if canisters are not properly cleaned before use. Additionally, all other sampling equipment (e.g., pump and flow controllers) should be thoroughly cleaned to ensure that the filling apparatus will not contaminate samples. Instructions for cleaning the canisters and certifying the field sampling system are described in Sections 12.1 and 12.2, respectively.

6.3 Because the GC-MS analytical system employs a Nafion® permeable membrane dryer to remove water vapor selectively from the sample stream, polar organic compounds may permeate concurrent with the moisture molecule. Consequently, the analyst should quantitate his or her system with the specific organic constituents under examination.

7. Apparatus

7.1 Sample Collection

[Note: Subatmospheric pressure and pressurized canister sampling systems are commercially available and have been used as part of U.S. Environmental Protection Agency's Toxics Air Monitoring Stations (TAMS), Urban Air Toxic Pollutant Program (UATP), and the non-methane organic compound (NMOC) sampling and analysis program.]

7.1.1 Subatmospheric Pressure (See Figure 2 Without Metal Bellows Type Pump)

7.1.1.1 Sampling inlet line - stainless steel tubing to connect the sampler to the sample inlet.

7.1.1.2 Sample canister - leak-free stainless steel pressure vessels of desired volume (e.g., 6 L), with valve and SUMMA® passivated interior surfaces (Scientific Instrumentation Specialists, Inc., P.O. Box 8941, Moscow, ID 83843, or Anderson Samplers, Inc., 4215-C Wendell Dr., Atlanta, GA, 30336, or equivalent).

7.1.1.3 Stainless steel vacuum/pressure gauge - capable of measuring vacuum (-100 to 0 kPa or 0 to 30 in Hg) and pressure (0-206 kPa or 0-30 psig) in the sampling system (Matheson, P.O. Box 136, Morrow, GA 30200, Model 63-3704, or equivalent). Gauges should be tested clean and leak tight.

7.1.1.4 Electronic mass flow controller - capable of maintaining a constant flow rate (± 10%) over a sampling period of up to 24 hours and under conditions of changing temperature (20-40°C) and humidity (Tylan Corp., 19220 S. Normandie Ave., Torrance, CA 90502, Model FC-260, or equivalent).

7.1.1.5 Particulate matter filter - 2-um sintered stainless steel in-line filter (Nupro Co., 4800 E. 345th St., Willoughby, OH 44094, Model SS-2F-K4-2, or equivalent).

7.1.1.6 Electronic timer - for unattended sample collection (Paragon Elect. Co., 606 Parkway Blvd., P.O. Box 28, Twin Rivers, WI 54201, Model 7008-00, or equivalent).

7.1.1.7 Solenoid valve - electrically-operated, bi-stable solenoid valve (Skinner Magnelatch Valve, New Britain, CT, Model V5RAM49710, or equivalent) with Viton® seat and o-rings.

7.1.1.8 Chromatographic grade stainless steel tubing and fittings - for interconnections (Alltech Associates, 2051 Waukegan Rd., Deerfield, IL 60015, Cat. #8125, or equivalent). All such materials in contact with sample, analyte, and support gases prior to analysis should be chromatographic grade stainless steel.

7.1.1.9 Thermostatically controlled heater - to maintain temperature inside insulated sampler enclosure above ambient temperature (Watlow Co., Pfafftown, NC, Part 04010080, or equivalent).

7.1.1.10 Heater thermostat - automatically regulates heater temperature (Elmwood Sensors, Inc., 500 Narragansett Park Dr., Pawtucket RI 02861, Model 3455-RC-0100-0222, or equivalent).

7.1.1.11 Fan - for cooling sampling system (EG&G Rotron, Woodstock, NY, Model SUZAI, or equivalent).

7.1.1.12 Fan thermostat - automatically regulates fan operation (Elmwood Sensors, Inc., Pawtucket, RI, Model 3455-RC-0100-0244, or equivalent).

7.1.1.13 Maximum-minimum thermometer - records highest and lowest temperatures during sampling period (Thomas Scientific, Brooklyn Thermometer Co., Inc., P/N 9327H30, or equivalent).

7.1.1.14 Nupro stainless steel shut-off valve - leak free, for vacuum/pressure gauge.

7.1.1.15 Auxiliary vacuum pump - continuously draws ambient air to be sampled through the inlet manifold at 10 L/min. or higher flow rate. Sample is extracted from the manifold at a lower rate, and excess air is exhausted. [Note: The use of higher inlet flow rates dilutes any contamination present in the inlet and reduces the possibility of sample contamination as a result of contact with active adsorption sites on inlet walls.]

7.1.1.16 Elapsed time meter - measures duration of sampling (Conrac, Cramer Div., Old Saybrook, CT, Type 6364, P/N 10082, or equivalent).

7.1.1.17 Optional fixed orifice, capillary, or adjustable micrometering valve - may be used in lieu of the electronic flow controller for grab samples or short duration time-integrated samples. Usually appropriate only in situations where screening samples are taken to assess future sampling activity.

7.1.2 Pressurized (Figure 2 With Metal Bellows Type Pump and Figure 3)

7.1.2.1 Sample pump - stainless steel, metal bellows type (Metal Bellows Corp., 1075 Providence Highway, Sharon, MA 02067, Model MB-151, or equivalent), capable of 2 atmospheres output pressure. Pump must be free of leaks, clean, and uncontaminated by oil or organic compounds. [Note: An alternative sampling system has been developed by Dr. R. Rasmussen, The Oregon Graduate Center (18,19) and is illustrated in Figure 3. This flow system uses, in order, a pump, a mechanical flow regulator, and a mechanical compensating flow restrictive device. In this configuration the pump is purged with a large sample flow, thereby eliminating the need for an auxiliary vacuum pump to flush the sample inlet. Interferences using this configuration have been minimal.]

7.1.2.2 Other supporting materials - all other components of the pressurized sampling system (Figure 2 with metal bellows type pump and Figure 3) are similar to components discussed in Sections 7.1.1.1 through 7.1.1.16.

7.2 Sample Analysis

7.2.1 GC-MS-SCAN Analytical System (See Figure 4)

7.2.1.1 The GC-MS-SCAN analytical system must be capable of acquiring and processing data in the MS-SCAN mode.

7.2.1.2 Gas chromatograph - capable of sub-ambient temperature programming for the oven, with other generally standard features such as gas flow regulators, automatic control of valves and integrator, etc. Flame ionization detector optional. (Hewlett Packard, Rt. 41, Avondale, PA 19311, Model 5880A, with oven temperature control and Level 4 BASIC programming, or equivalent.)

7.2.1.3 Chromatographic detector - mass-selective detector (Hewlett Packard, 3000-T Hanover St., 9B, Palo Alto, CA 94304, Model HP-5970 MS, or equivalent), equipped with computer and appropriate software (Hewlett Packard, 3000-T Hanover St., 9B, Palo Alto, CA 94304, HP-216 Computer, Quicksilver MS software, Pascal 3.0, mass storage 9133 HP Winchester with 3.5 inch floppy disk, or equivalent). The GC-MS is set in the SCAN mode, where the MS screens the sample for identification and quantitation of VOC species.

7.2.1.4 Cryogenic trap with temperature control assembly - refer to Section 10.1.1.3 for complete description of trap and temperature control assembly (Nutech Corporation, 2142 Geer St., Durham, NC, 27704, Model 320-01, or equivalent).

7.2.1.5 Electronic mass flow controllers (3) - maintain constant flow (for carrier gas and sample gas) and to provide analog output to monitor flow anomalies (Tylan Model 260, 0-100 cm^3/min, or equivalent).

7.2.1.6 Vacuum pump - general purpose laboratory pump, capable of drawing the desired sample volume through the cryogenic trap (Thomas Industries, Inc., Sheboygan, WI, Model 107BA20, or equivalent).

7.2.1.7 Chromatographic grade stainless steel tubing and stainless steel plumbing fittings - refer to Section 7.1.1.8 for description.

7.2.1.8 Chromatographic column - to provide compound separation such as shown in Table 5 (Hewlett Packard, Rt. 41, Avondale, PA 19311, OV-1 capillary column, 0.32 mm x 50 m with 0.88 um crosslinked methyl silicone coating, or equivalent).

7.2.1.9 Stainless steel vacuum/pressure gauge (optional) - capable of measuring vacuum (-101.3 to 0 kPa) and pressure (0-206 kPa) in the sampling system (Matheson, P.O. Box 136, Morrow, GA 30200, Model 63-3704, or equivalent). Gauges should be tested clean and leak tight.

7.2.1.10 Stainless steel cylinder pressure regulators - standard, two-stage cylinder regulators with pressure gauges for helium, zero air and hydrogen gas cylinders.

7.2.1.11 Gas purifiers (3) - used to remove organic impurities and moisture from gas streams (Hewlett Packard, Rt. 41, Avondale, PA, 19311, P/N 19362 - 60500, or equivalent).

7.2.1.12 Low dead-volume tee (optional) - used to split the exit flow from the GC column (Alltech Associates, 2051 Waukegan Rd., Deerfield, IL 60015, Cat. #5839, or equivalent).

7.2.1.13 Nafion® dryer - consisting of Nafion tubing coaxially mounted within larger tubing (Perma Pure Products, 8 Executive Drive, Toms River, NJ, 08753, Model MD-125-48, or equivalent). Refer to Section 10.1.1.2 for description.

7.2.1.14 Six-port gas chromatographic valve - (Seismograph Service Corp, Tulsa, OK, Seiscor Model VIII, or equivalent).

7.2.1.15 Chart recorder (optional) - compatible with the detector output signals to record optional FID detector response to the sample.

7.2.1.16 Electronic integrator (optional) - compatible with the detector output signal of the FID and capable of integrating the area of one or more response peaks and calculating peak areas corrected for baseline drift.

7.2.2 GC-MS-SIM Analytical System (See Figure 4)

7.2.2.1 The GC-MS-SIM analytical system must be capable of acquiring and processing data in the MS-SIM mode.

7.2.2.2 All components of the GC-MS-SIM system are identical to Sections 7.2.1.2 through 7.2.1.16.

7.2.3 GC-Multidetector Analytical System (See Figure 5 and Figure 6)

7.2.3.1 Gas chromatograph with flame ionization and electron capture detectors (photoionization detector optional) - capable of sub-ambient temperature programming for the oven and simultaneous operation of all detectors, and with other generally standard features such as gas flow regulators, automatic control of valves and integrator, etc. (Hewlett Packard, Rt. 41, Avondale, PA 19311, Model 5880A, with oven temperature control and Level 4 BASIC programming, or equivalent).

7.2.3.2 Chart recorders - compatible with the detector output signals to record detector response to the sample.

7.2.3.3 Electronic integrator - compatible with the detector output signals and capable of integrating the area of one or more response peaks and calculating peak areas corrected for baseline drift.

7.2.3.4 Six-port gas chromatographic valve - (Seismograph Service Corp, Tulsa, OK, Seiscor Model VIII, or equivalent).

7.2.3.5 Cryogenic trap with temperature control assembly - refer to Section 10.1.1.3 for complete description of trap and temperature control assembly (Nutech Corporation, 2142 Geer St., Durham, NC 27704, Model 320-01, or equivalent).

7.2.3.6 Electronic mass flow controllers (3) - maintain constant flow (for carrier gas, nitrogen make-up gas and sample gas) and to provide analog output to monitor flow anomalies (Tylan Model 260, 0-100 cm^3/min, or equivalent).

7.2.3.7 Vacuum pump - general purpose laboratory pump, capable of drawing the desired sample volume through the cryogenic trap (see 7.2.1.6 for source and description).

7.2.3.8 Chromatographic grade stainless steel tubing and stainless steel plumbing fittings - refer to Section 7.1.1.8 for description.

7.2.3.9 Chromatographic column - to provide compound separation such as shown in Table 7. (Hewlett Packard, Rt. 41, Avondale, PA 19311, OV-1 capillary column, 0.32 mm x 50 m with 0.88 um crosslinked methyl silicone coating, or equivalent). [Note: Other columns (e.g., DB-624) can be used as long as the system meets user needs. The wider Megabore® column (i.e., 0.53 mm I.D.) is less susceptible to plugging as a result of trapped water, thus eliminating the need for a Nafion® dryer in the analytical system. The Megabore® column has sample capacity approaching that of a packed column, while retaining much of the peak resolution traits of narrower columns (i.e., 0.32 mm I.D.).

7.2.3.10 Vacuum/pressure gauges (3) - refer to Section 7.2.1.9 for description.

7.2.3.11 Cylinder pressure stainless steel regulators - standard, two-stage cylinder regulators with pressure gauges for helium, zero air, nitrogen, and hydrogen gas cylinders.

7.2.3.12 Gas purifiers (4) - used to remove organic impurities and moisture from gas streams (Hewlett-Packard, Rt. 41, Avondale, PA, 19311, P/N 19362 - 60500, or equivalent).

7.2.3.13 Low dead-volume tee - used to split (50/50) the exit flow from the GC column (Alltech Associates, 2051 Waukegan Rd., Deerfield, IL 60015, Cat. #5839, or equivalent).

7.3 Canister Cleaning System (See Figure 7)

7.3.1 Vacuum pump - capable of evacuating sample canister(s) to an absolute pressure of <0.05 mm Hg.

7.3.2 Manifold - stainless steel manifold with connections for simultaneously cleaning several canisters.

7.3.3 Shut-off valve(s) - seven (7) on-off toggle valves.

7.3.4 Stainless steel vacuum gauge - capable of measuring vacuum in the manifold to an absolute pressure of 0.05 mm Hg or less.

7.3.5 Cryogenic trap (2 required) - stainless steel U-shaped open tubular trap cooled with liquid oxygen or argon to prevent contamination from back diffusion of oil from vacuum pump and to provide clean, zero air to sample canister(s).

7.3.6 Stainless steel pressure gauges (2) - 0-345 kPa (0-50 psig) to monitor zero air pressure.

7.3.7 Stainless steel flow control valve - to regulate flow of zero air into canister(s).

7.3.8 Humidifier - pressurizable water bubbler containing high performance liquid chromatography (HPLC) grade deionized water or other system capable of providing moisture to the zero air supply.

7.3.9 Isothermal oven (optional) for heating canisters (Fisher Scientific, Pittsburgh, PA, Model 349, or equivalent).

7.4 Calibration System and Manifold (See Figure 8)

7.4.1 Calibration manifold - glass manifold, (1.25 cm I.D. x 66 cm) with sampling ports and internal baffles for flow disturbance to ensure proper mixing.

7.4.2 Humidifier - 500-mL impinger flask containing HPLC grade deionized water.

7.4.3 Electronic mass flow controllers - one 0 to 5 L/min and one 0 to 50 cm^3/min (Tylan Corporation, 23301-TS Wilmington Ave., Carson, CA, 90745, Model 2160, or equivalent).

7.4.4 Teflon® filter(s) - 47-mm Teflon® filter for particulate control, best source.

8. Reagents and Materials

8.1 Gas cylinders of helium, hydrogen, nitrogen, and zero air - ultrahigh purity grade, best source.

8.2 Gas calibration standards - cylinder(s) containing approximately 10 ppmv of each of the following compounds of interest:

vinyl chloride
vinylidene chloride
1,1,2-trichloro-1,2,2-trifluoroethane
chloroform
1,2-dichloroethane
benzene
toluene
Freon 12
methyl chloride
1,2-dichloro-1,1,2,2-tetrafluoroethane
methyl bromide
ethyl chloride
Freon 11
dichloromethane
1,1-dichloroethane
cis-1,2-dichloroethylene
1,2-dichloropropane
1,1,2-trichloroethane
1,2-dibromoethane
tetrachloroethylene
chlorobenzene
benzyl chloride
hexachloro-1,3-butadiene
methyl chloroform
carbon tetrachloride
trichloroethylene
cis-1,3-dichloropropene
trans-1,3-dichloropropene
ethylbenzene
o-xylene
m-xylene
p-xylene
styrene
1,1,2,2-tetrachloroethane
1,3,5-trimethylbenzene
1,2,4-trimethylbenzene
m-dichlorobenzene
o-dichlorobenzene
p-dichlorobenzene
1,2,4-trichlorobenzene

The cylinder(s) should be traceable to a National Bureau of Standards (NBS) Standard Reference Material (SRM) or to a NBS/EPA approved Certified Reference Material (CRM). The components may be purchased in one cylinder or may be separated into different cylinders. Refer to manufacturer's specification for guidance on purchasing and mixing VOCs in gas cylinders. Those compounds purchased should match one's own target list.

8.3 Cryogen - liquid oxygen (bp -183.0°C), or liquid argon (bp -185.7°C), best source.

8.4 Gas purifiers - connected in-line between hydrogen, nitrogen, and zero air gas cylinders and system inlet line, to remove moisture and organic impurities from gas streams (Alltech Associates, 2051 Waukegan Road, Deerfield, IL, 60015, or equivalent).

8.5 Deionized water - high performance liquid chromatography (HPLC) grade, ultrahigh purity (for humidifier), best source.

8.6 4-bromofluorobenzene - used for tuning GC-MS, best source.

8.7 Hexane - for cleaning sampling system components, reagent grade, best source.

8.8 Methanol - for cleaning sampling system components, reagent grade, best source.

9. Sampling System

9.1 System Description

9.1.1 Subatmospheric Pressure Sampling [See Figure 2 (Without Metal Bellows Type Pump)]

9.1.1.1 In preparation for subatmospheric sample collection in a canister, the canister is evacuated to 0.05 mm Hg. When opened to the atmosphere containing the VOCs to be sampled, the differential pressure causes the sample to flow into the canister. This technique may be used to collect grab samples (duration of 10 to 30 seconds) or time-integrated samples (duration of 12 to 24 hours) taken through a flow-restrictive inlet (e.g., mass flow controller, critical orifice).

9.1.1.2 With a critical orifice flow restrictor, there will be a decrease in the flow rate as the pressure approaches atmospheric. However, with a mass flow controller, the subatmospheric sampling system can maintain a constant flow rate from full vacuum to within about 7 kPa (1.0 psi) or less below ambient pressure.

9.1.2 Pressurized Sampling [See Figure 2 (With Metal Bellows Type Pump)]

9.1.2.1 Pressurized sampling is used when longer-term integrated samples or higher volume samples are required. The sample is collected in a canister using a pump and flow control arrangement to achieve a typical 103-206 kPa (15-30 psig) final canister pressure. For example, a 6-liter evacuated canister can be filled at 10 cm^3/min for 24 hours to achieve a final pressure of about 144 kPa (21 psig).

9.1.2.2 In pressurized canister sampling, a metal bellows type pump draws in ambient air from the sampling manifold to fill and pressurize the sample canister.

9.1.3 All Samplers

9.1.3.1 A flow control device is chosen to maintain a constant flow into the canister over the desired sample period. This flow rate is determined so the canister is filled (to about 88.1 kPa for subatmospheric pressure sampling or to about one atmosphere above ambient pressure for pressurized sampling) over the desired sample period. The flow rate can be calculated by

$$F = \frac{P \times V}{T \times 60}$$

where:

F = flow rate (cm^3/min).

P = final canister pressure, atmospheres absolute. P is approximately equal to

$$\frac{\text{kPa gauge}}{101.2} + 1$$

V = volume of the canister (cm^3).

T = sample period (hours).

For example, if a 6-L canister is to be filled to 202 kPa (2 atmospheres) absolute pressure in 24 hours, the flow rate can be calculated by

$$F = \frac{2 \times 6000}{24 \times 60} = 8.3 \text{ cm}^3/\text{min}$$

9.1.3.2 For automatic operation, the timer is wired to start and stop the pump at appropriate times for the desired sample period. The timer must also control the solenoid valve, to open the valve when starting the pump and close the valve when stopping the pump.

9.1.3.3 The use of the Skinner Magnelatch valve avoids any substantial temperature rise that would occur with a conventional, normally closed solenoid valve that would have to be energized during the entire sample period. The temperature rise in the valve could cause outgassing of organic compounds from the Viton valve seat material. The Skinner Magnelatch valve requires only a brief electrical pulse to open or close at the appropriate start and stop times and therefore experiences no temperature increase. The pulses may be obtained either with an electronic timer that can be programmed for short (5 to 60 seconds) ON periods, or with a conventional mechanical timer and a special pulse circuit. A simple electrical pulse circuit for operating the Skinner Magnelatch solenoid valve with a conventional mechanical timer is illustrated in Figure 9(a). However, with this simple circuit, the valve may operate unreliably during brief power interruptions or if the timer is manually switched on and off too fast. A better circuit incorporating a time-delay relay to provide more reliable valve operation is shown in Figure 9(b).

9.1.3.4 The connecting lines between the sample inlet and the canister should be as short as possible to minimize their volume. The flow rate into the canister should remain relatively constant over the entire sampling period. If a critical orifice is used, some drop in the flow rate may occur near the end of the sample period as the canister pressure approaches the final calculated pressure.

9.1.3.5 As an option, a second electronic timer (see Section 7.1.1.6) may be used to start the auxiliary pump several hours prior to the sampling period to flush and condition the inlet line.

9.1.3.6 Prior to field use, each sampling system must pass a humid zero air certification (see Section 12.2.2). All plumbing should be checked carefully for leaks. The canisters must also pass a humid zero air certification before use (see Section 12.1).

9.2 Sampling Procedure

9.2.1 The sample canister should be cleaned and tested according to the procedure in Section 12.1.

9.2.2 A sample collection system is assembled as shown in Figure 2 (and Figure 3) and must meet certification requirements as outlined in Section 12.2.3. [Note: The sampling system should be contained in an appropriate enclosure.]

9.2.3 Prior to locating the sampling system, the user may want to perform "screening analyses" using a portable GC system, as outlined in Appendix B, to determine potential volatile organics present and potential "hot spots." The information gathered from the portable GC screening analysis would be used in developing a monitoring protocol, which includes the sampling system location, based upon the "screening analysis" results.

9.2.4 After "screening analysis," the sampling system is located. Temperatures of ambient air and sampler box interior are recorded on canister sampling field data sheet (Figure 10). [Note: The following discussion is related to Figure 2.]

9.2.5 To verify correct sample flow, a "practice" (evacuated) canister is used in the sampling system. [Note: For a subatmospheric sampler, the flow meter and practice canister are needed. For the pump-driven system, the practice canister is not needed, as the flow can be measured at the outlet of the system.] A certified mass flow meter is attached to the inlet line of the manifold, just in front of the filter. The canister is opened. The sampler is turned on and the reading of the certified mass flow meter is compared to the sampler mass flow controller. The values should agree within ±10%. If not, the sampler mass flow meter needs to be recalibrated or there is a leak in the system. This should be investigated and corrected. [Note: Mass flow meter readings may drift. Check the zero reading carefully and add or subtract the zero reading when reading or adjusting the sampler flow rate, to compensate for any zero drift.] After two minutes, the desired canister flow rate is adjusted to the proper value (as indicated by the certified mass flow meter) by the sampler flow control unit controller (e.g., 3.5 cm^3/min for 24 hr, 7.0 cm^3/min for 12 hr). Record final flow under "CANISTER FLOW RATE," Figure 10.

9.2.6 The sampler is turned off and the elapsed time meter is reset to 000.0. Note: Any time the sampler is turned off, wait at least 30 seconds to turn the sampler back on.

9.2.7 The "practice" canister and certified mass flow meter are disconnected and a clean certified (see Section 12.1) canister is attached to the system.

9.2.8 The canister valve and vacuum/pressure gauge valve are opened.

9.2.9 Pressure/vacuum in the canister is recorded on the canister sampling field data sheet (Figure 10) as indicated by the sampler vacuum/pressure gauge.

9.2.10 The vacuum/pressure gauge valve is closed and the maximum-minimum thermometer is reset to current temperature. Time of day and elapsed time meter readings are recorded on the canister sampling field data sheet.

9.2.11 The electronic timer is set to begin and stop the sampling period at the appropriate times. Sampling commences and stops by the programmed electronic timer.

9.2.12 After the desired sampling period, the maximum, minimum, current interior temperature and current ambient temperature are recorded on the sampling field data sheet. The current reading from the flow controller is recorded.

9.2.13 At the end of the sampling period, the vacuum/pressure gauge valve on the sampler is briefly opened and closed and the pressure/vacuum is recorded on the sampling field data sheet. Pressure should be close to desired pressure. [Note: For a subatmospheric sampling system, if the canister is at atmospheric pressure when the field final pressure check is performed, the sampling period may be suspect. This information should be noted on the sampling field data sheet.] Time of day and elapsed time meter readings are also recorded.

9.2.14 The canister valve is closed. The sampling line is disconnected from the canister and the canister is removed from the system. For a subatmospheric system, a certified mass flow meter is once again connected to the inlet manifold in front of the in-line filter and a "practice" canister is attached to the Magnelatch valve of the sampling system. The final flow rate is recorded on the canister sampling field data sheet (see Figure 10). [Note: For a pressurized system, the final flow may be measured directly.] The sampler is turned off.

9.2.15 An identification tag is attached to the canister. Canister serial number, sample number, location, and date are recorded on the tag.

10. Analytical System (See Figures 4, 5 and 6)

10.1 System Description

10.1.1 GC-MS-SCAN System

10.1.1.1 The analytical system is comprised of a GC equipped with a mass-selective detector set in the SCAN mode (see Figure 4). All ions are scanned by the MS repeatedly during the

GC run. The system includes a computer and appropriate software for data acquisition, data reduction, and data reporting. A 400 cm^3 air sample is collected from the canister into the analytical system. The sample air is first passed through a Nafion® dryer, through the 6-port chromatographic valve, then routed into a cryogenic trap. [Note: While the GC-multidetector analytical system does not employ a Nafion® dryer for drying the sample gas stream, it is used here because the GC-MS system utilizes a larger sample volume and is far more sensitive to excessive moisture than the GC-multidetector analytical system. Moisture can adversely affect detector precision. The Nafion® dryer also prevents freezing of moisture on the 0.32 mm I.D. column, which may cause column blockage and possible breakage.] The trap is heated (-160°C to 120°C in 60 sec) and the analyte is injected onto the OV-1 capillary column (0.32 mm x 50 m). [Note: Rapid heating of the trap provides efficient transfer of the sample components onto the gas chromatographic column.] Upon sample injection onto the column, the MS computer is signaled by the GC computer to begin detection of compounds which elute from the column. The gas stream from the GC is scanned within a preselected range of atomic mass units (amu). For detection of compounds in Table 1, the range should be 18 to 250 amu, resulting in a 1.5 Hz repetition rate. Six (6) scans per eluting chromatographic peak are provided at this rate. The 10-15 largest peaks are chosen by an automated data reduction program, the three scans nearest the peak apex are averaged, and a background subtraction is performed. A library search is then performed and the top ten best matches for each peak are listed. A qualitative characterization of the sample is provided by this procedure. A typical chromatogram of VOCs determined by GC-MS-SCAN is illustrated in Figure 11(a).

10.1.1.2 A Nafion® permeable membrane dryer is used to remove water vapor selectively from the sample stream. The permeable membrane consists of Nafion® tubing (a copolymer of tetrafluoroethylene and fluorosulfonyl monomer) that is coaxially mounted within larger tubing. The sample stream is passed through the interior of the Nafion® tubing, allowing water (and other light, polar compounds) to permeate through the walls into a dry air purge stream flowing through the annular space between the Nafion® and outer tubing. [Note: To prevent excessive moisture build-up and any memory effects in the dryer, a clean-up procedure involving periodic heating of the dryer (100°C for 20 minutes) while purging with dry zero air (500 cm^3/min) should be implemented as part of the user's SOP manual. The clean-up procedure is repeated during each analysis (see Section 14, reference 7). Recent studies have indicated no substantial loss of targeted VOCs utilizing the above clean-up procedure (7). This cleanup procedure is particularly useful when employing cryogenic preconcentration of VOCs with subsequent GC analysis using a 0.32 mm I.D. column because excess accumulated water can cause trap and column blockage and also adversely affect detector precision. In addition, the improvement in water removal from the sampling stream will allow analyses of much larger volumes of sample air in the event that greater system sensitivity is required for targeted compounds.]

10.1.1.3 The packed metal tubing used for reduced temperature trapping of VOCs is shown in Figure 12. The cooling unit is comprised of a 0.32 cm outside diameter (O.D.) nickel tubing loop packed with 60-80 mesh Pyrex® beads (Nutech Model 320-01, or equivalent). The nickel tubing loop is wound onto a cylindrically formed tube heater (250 watt). A cartridge heater (25 watt) is sandwiched between pieces of aluminum plate at the trap inlet and outlet to provide additional heat to eliminate cold spots in the transfer tubing. During operation, the trap is inside a two-section stainless steel shell which is well insulated. Rapid heating (-150 to +100°C in 55 s) is accomplished by direct thermal contact between the heater and the trap tubing. Cooling is achieved by vaporization of the cryogen. In the shell, efficient cooling (+120 to -150°C in 225 s) is facilitated by confining the vaporized cryogen to the small open volume surrounding the trap assembly. The trap assembly and chromatographic valve are mounted on a baseplate fitted into the injection and auxiliary zones of the GC on an insulated pad directly above the column oven when used with the Hewlett-Packard 5880 GC. [Note: Alternative trap assembly and connection to the GC may be used depending upon user's requirements.] The carrier gas line is connected to the injection end of the analytical column with a zero-dead-volume fitting that is usually held in the heated zone above the GC oven. A 15 cm x 15 cm x 24 cm aluminum box is fitted over the sample handling elements to complete the package. Vaporized cryogen is vented through the top of the box.

10.1.1.4 As an option, the analyst may wish to split the gas stream exiting the column with a low dead-volume tee, passing one-third of the sample gas (1.0 mL/min) to the mass-selective detector and the remaining two-thirds (2.0 mL/min) through a flame ionization detector, as illustrated as an option in Figure 4. The use of the specific detector (MS-SCAN) coupled with the non-specific detector (FID) enables enhancement of data acquired from a single analysis. In particular, the FID provides the user:

- Semi-real time picture of the progress of the analytical scheme;
- Confirmation by the concurrent MS analysis of other labs that can provide only FID results; and
- Ability to compare GC-FID with other analytical laboratories with only GC-FID capability.

10.1.2 GC-MS-SIM System

10.1.2.1 The analytical system is comprised of a GC equipped with an OV-1 capillary column (0.32 mm x 50 m) and a mass-selective detector set in the SIM mode (see Figure 4). The GC-MS is set up for automatic, repetitive analysis. The system is programmed to acquire data for only the target compounds and to disregard all others. The sensitivity is 0.1 ppbv for a 250 cm^3 air sample with analytical precision of about 5% relative standard deviation. Concentration of compounds based upon a previously installed calibration table is reported by an automated data reduction program. A Nafion® dryer is also employed by this analytical system prior to cryogenic preconcentration; therefore, many polar compounds are not identified by this procedure.

10.1.2.2 SIM analysis is based on a combination of retention times and relative abundances of selected ions (see Table 2). These qualifiers are stored on the hard disk of the GC-MS computer and are applied for identification of each chromatographic peak. The retention time qualifier is determined to be ± 0.10 minute of the library retention time of the compound. The acceptance level for relative abundance is determined to be ± 15% of the expected abundance, except for vinyl chloride and methylene chloride, which is determined to be ± 25%. Three ions are measured for most of the forty compounds. When compound identification is made by the computer, any peak that fails any of the qualifying tests is flagged (e.g., with an *). All the data should be manually examined by the analyst to determine the reason for the flag and whether the compound should be reported as found. While this adds some subjective judgment to the analysis, computer-generated identification problems can be clarified by an experienced operator. Manual inspection of the quantitative results should also be performed to verify concentrations outside the expected range. A typical chromatogram of VOCs determined by GC-MS-SIM mode is illustrated in Figure 11(b).

10.1.3 GC-Multidetector (GC-FID-ECD) System with Optional PID

10.1.3.1 The analytical system (see Figure 5) is comprised of a gas chromatograph equipped with a capillary column and electron capture and flame ionization detectors (see Figure 5). In typical operation, sample air from pressurized canisters is vented past the inlet to the analytical system from the canister at a flow rate of 75 cm^3/min. For analysis, only 35 cm^3/min of sample gas is used, while excess is vented to the atmosphere. Sub-ambient pressure canisters are connected directly to the inlet. The sample gas stream is routed through a six port chromatographic valve and into the cryogenic trap for a total sample volume of 490 cm^3. [Note: This represents a 14 minute sampling period at a rate of 35 cm^3/min.] The trap (see Section 10.1.1.3) is cooled to -150°C by controlled release of a cryogen. VOCs and SVOCs are condensed on the trap surface while N_2, O_2, and other sample components are passed to the pump. After the organic compounds are concentrated, the valve is switched and the trap is heated. The revolatilized compounds are transported by helium carrier gas at a rate of 4 cm^3/min to the head of the Megabore® OV-1 capillary column (0.53 mm x 30 m). Since the column initial temperature is at -50°C, the VOCs and SVOCs are cryofocussed on the head of the column. Then, the oven temperature is programmed to increase and the VOCs/SVOCs in the carrier gas are chromatographically separated. The carrier gas containing the separated VOCs/SVOCs is then directed to two parallel detectors at a flow rate of 2 cm^3/min each. The detectors sense the presence of the speciated VOCs/SVOCs, and the response is recorded by either a strip chart recorder or a data processing unit.

10.1.3.2 Typical chromatograms of VOCs determined by the GC-FID-ECD analytical system are illustrated in Figures 11(c) and 11(d), respectively.

10.1.3.3 Helium is used as the carrier gas (4 cm^3/min) to purge residual air from the trap at the end of the sampling phase and to carry the revolatilized VOCs through the Megabore® GC column. Moisture and organic impurities are removed from the helium gas stream by a chemical purifier installed in the GC (see

Section 7.2.1.11). After exiting the OV-1 Megabore® column, the carrier gas stream is split to the two detectors at rates of 2 cm^3/min each.

10.1.3.4 Gas scrubbers containing Drierite® or silica gel and 5A molecular sieve are used to remove moisture and organic impurities from the zero air, hydrogen, and nitrogen gas streams. [Note: Purity of gas purifiers is checked prior to use by passing humid zero-air through the gas purifier and analyzing according to Section 12.2.2.]

10.1.3.5 All lines should be kept as short as practical. All tubing used for the system should be chromatographic grade stainless steel connected with stainless steel fittings. After assembly, the system should be checked for leaks according to manufacturer's specifications.

10.1.3.6 The FID burner air, hydrogen, nitrogen (make-up), and helium (carrier) flow rates should be set according to the manufacturer's instructions to obtain an optimal FID response while maintaining a stable flame throughout the analysis. Typical flow rates are: burner air, 450 cm^3/min; hydrogen, 30 cm^3/min; nitrogen, 30 cm^3/min; helium, 2 cm^3/min.

10.1.3.7 The ECD nitrogen make-up gas and helium carrier flow rates should be set according to manufacturer's instructions to obtain an optimal ECD response. Typical flow rates are: nitrogen, 76 cm^3/min and helium, 2 cm^3/min.

10.1.3.8 The GC-FID-ECD could be modified to include a PID (see Figure 6) for increased sensitivity (20). In the photoionization process, a molecule is ionized by ultraviolet light as follows: R + hv --> R + e-, where R+ is the ionized species and a photon is represented by hv, with energy less than or equal to the ionization potential of the molecule. Generally all species with an ionization potential less than the ionization energy of the lamp are detected. Because the ionization potential of all major components of air (O_2, N_2, CO, CO_2, and H_2O) is greater than the ionization energy of lamps in general use, they are not detected. The sensor is comprised of an argon-filled, ultraviolet (UV) light source where a portion of the organic vapors are ionized in the gas stream. A pair of electrodes are contained in a chamber adjacent to the sensor. When a positive potential is applied to the electrodes, any ions formed by the absorption of UV light are driven by the created electronic field to the cathode, and the current (proportional to the organic vapor concentration) is measured. The PID is generally used for compounds having ionization potentials less than the ratings of the ultraviolet lamps. This detector is used for determination of most chlorinated and oxygenated hydrocarbons, aromatic compounds, and high molecular weight aliphatic compounds. Because the PID is insensitive to methane, ethane, carbon monoxide, carbon dioxide, and water vapor, it is an excellent detector. The electron volt rating is applied specifically to the wavelength of the most intense emission line of the lamp's output spectrum. Some compounds with ionization potentials above the lamp rating can still be detected due to the presence of small quantities of more intense light. A typical system configuration associated with the GC-FID-ECD-PID is illustrated in Figure 6. This system is currently being used in EPA's FY-88 Urban Air Toxics Monitoring Program.

10.2 GC-MS-SCAN-SIM System Performance Criteria

10.2.1 GC-MS System Operation

10.2.1.1 Prior to analysis, the GC-MS system is assembled and checked according to manufacturer's instructions.

10.2.1.2 Table 3.0 outlines general operating conditions for the GC-MS-SCAN-SIM system with optional FID.

10.2.1.3 The GC-MS system is first challenged with humid zero air (see Section 11.2.2).

10.2.1.4 The GC-MS and optional FID system is acceptable if it contains less than 0.2 ppbv of targeted VOCs.

10.2.2 Daily GC-MS Tuning (See Figure 13)

10.2.2.1 At the beginning of each day or prior to a calibration, the GC-MS system must be tuned to verify that acceptable performance criteria are achieved.

10.2.2.2 For tuning the GC-MS, a cylinder containing 4-bromofluorobenzene is introduced via a sample loop valve injection system. [Note: Some systems allow auto-tuning to facilitate this process.] The key ions and ion abundance criteria that must be met are illustrated in Table 4. Analysis should not begin until all those criteria are met.

10.2.2.3 The GC-MS tuning standard could also be used to assess GC column performance (chromatographic check) and as an internal standard. Obtain a background correction mass spectra of 4-bromofluorobenzene and check that all key ions criteria are met. If the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are achieved.

10.2.2.4 The performance criteria must be achieved before any samples, blanks or standards are analyzed. If any key ion abundance observed for the daily 4-bromofluorobenzene mass tuning check differs by more than 10% absolute abundance from that observed during the previous daily tuning, the instrument must be retuned or the sample and/or calibration gases reanalyzed until the above condition is met.

10.2.3 GC-MS Calibration (See Figure 13)

[Note: Initial and routine calibration procedures are illustrated in Figure 13.]

10.2.3.1 Initial Calibration - Initially, a multipoint dynamic calibration (three levels plus humid zero air) is performed on the GC-MS system, before sample analysis, with the assistance of a calibration system (see Figure 8). The calibration system uses NBS traceable standards or NBS/EPA CRMs in pressurized cylinders [containing a mixture of the targeted VOCs at nominal concentrations of 10 ppmv in nitrogen (Section 8.2)] as working standards to be diluted with humid zero air. The contents of the working standard cylinder(s) are metered (2 cm^3/min) into the heated mixing chamber where they are mixed with a 2-L/min humidified zero air gas stream to achieve a nominal 10 ppbv per compound calibration mixture (see Figure 8). This nominal 10 ppbv standard mixture is allowed to flow and equilibrate for a minimum of 30 minutes. After the equilibration period, the gas standard mixture is sampled and analyzed by the real-time GC-MS system [see Figure 8(a) and Section 7.2.1]. The results of the analyses are averaged, flow audits are performed on the mass flow meters and the calculated concentration compared to generated values. After the GC-MS is calibrated at three concentration levels, a second humid zero air sample is passed through the system and analyzed. The second humid zero air test is used to verify that the GC-MS system is certified clean (less than 0.2 ppbv of target compounds).

10.2.3.2 As an alternative, a multipoint humid static calibration (three levels plus zero humid air) can be performed on the GC-MS system. During the humid static calibration analyses, three (3) SUMMA® passivated canisters are filled each at a different concentration between 1-20 ppbv from the calibration manifold using a pump and mass flow control arrangement [see Figure 8(c)]. The canisters are then delivered to the GC-MS to serve as calibration standards. The canisters are analyzed by the MS in the SIM mode, each analyzed twice. The expected retention time and ion abundance (see Table 2 and Table 5) are used to verify proper operation of the GC-MS system. A calibration response factor is determined for each analyte, as illustrated in Table 5, and the computer calibration table is updated with this information, as illustrated in Table 6.

10.2.3.3 Routine Calibration - The GC-MS system is calibrated daily (and before sample analysis) with a one-point calibration. The GC-MS system is calibrated either with the dynamic calibration procedure [see Figure 8(a)] or with a 6-L SUMMA® passivated canister filled with humid calibration standards from the calibration manifold (see Section 10.2.3.2). After the single point calibration, the GC-MS analytical system is challenged with a humidified zero gas stream to insure the analytical system returns to specification (less than 0.2 ppbv of selective organics).

10.3 GC-FID-ECD System Performance Criteria (With Optional PID System) (See Figure 14)

10.3.1 Humid Zero Air Certification

10.3.1.1 Before system calibration and sample analysis, the GC-FID-ECD analytical system is assembled and checked according to manufacturer's instructions.

10.3.1.2 The GC-FID-ECD system is first challenged with humid zero air (see Section 12.2.2) and monitored.

10.3.1.3 Analytical systems contaminated with less than 0.2 ppbv of targeted VOCs are acceptable.

10.3.2 GC Retention Time Windows Determination (See Table 7)

10.3.2.1 Before analysis can be performed, the retention time windows must be established for each analyte.

10.3.2.2 Make sure the GC system is within optimum operating conditions.

10.3.2.3 Make three injections of the standard containing all compounds for retention time window determination. [Note: The retention time window must be established for each analyte every 72 hours during continuous operation.]

10.3.2.4 Calculate the standard deviation of the three absolute retention times for each single component standard. The retention window is defined as the mean plus or minus three times the standard deviation of the individual retention times for each standard. In those cases where the standard deviation for a particular standard is zero, the laboratory must substitute the standard deviation of a closely-eluting, similar compound to develop a valid retention time window.

10.3.2.5 The laboratory must calculate retention time windows for each standard (see Table 7) on each GC column, whenever a new GC column is installed or when major components of the GC are changed. The data must be noted and retained in a notebook by the laboratory as part of the user SOP and as a quality assurance check of the analytical system.

10.3.3 GC Calibration

[Note: Initial and routine calibration procedures are illustrated in Figure 14.]

10.3.3.1 Initial Calibration - Initially, a multipoint dynamic calibration (three levels plus humid zero air) is performed on the GC-FID-ECD system, before sample analysis, with the assistance of a calibration system (see Figure 8). The calibration system uses NBS traceable standards or NBS/EPA CRMs in pressurized cylinders [containing a mixture of the targeted VOCs at nominal concentrations of 10 ppmv in nitrogen (Section 8.2)] as working standards to be diluted with humid zero air. The contents of the working standard cylinders are metered (2 cm^3/min) into the heated mixing chamber where they are mixed with a 2-L/min humidified zero air stream to achieve a nominal 10 ppbv per compound calibration mixture (see Figure 8). This nominal 10 ppbv standard mixture is allowed to flow and equilibrate for an appropriate amount of time. After the equilibration period, the gas standard mixture is sampled and analyzed by the GC-MS system [see Figure 8(a)]. The results of the analyses are averaged, flow audits are performed on the mass flow controllers used to generate the standards and the appropriate response factors (concentration/area counts) are calculated for each compound, as illustrated in Table 5. [Note: GC-FIDs are linear in the 1-20 ppbv range and may not require repeated multipoint calibrations; whereas, the GC-ECD will require frequent linearity evaluation.] Table 5 outlines typical calibration response factors and retention times for 40 VOCs. After the GC-FID-ECD is calibrated at the three concentration levels, a second humid zero air sample is passed through the system and analyzed. The second humid zero air test is used to verify that the GC-FID-ECD system is certified clean (less than 0.2 ppbv of target compounds).

10.3.3.2 Routine Calibration - A one point calibration is performed daily on the analytical system to verify the initial multipoint calibration (see Section 10.3.3.1). The analyzers (GC-FID-ECD) are calibrated (before sample analysis) using the static calibration procedures (see Section 10.2.3.2) involving pressurized gas cylinders containing low concentrations of the targeted VOCs (10 ppbv) in nitrogen. After calibration, humid zero air is once again passed through the analytical system to verify residual VOCs are not present.

10.3.4 GC-FID-ECD-PID System Performance Criteria

10.3.4.1 As an option, the user may wish to include a photoionization detector (PID) to assist in peak identification and increase sensitivity.

10.3.4.2 This analytical system is presently being used in U.S. Environmental Protection Agency's Urban Air Toxic Pollutant Program (UATP).

10.3.4.3 Preparation of the GC-FID-ECD-PID analytical system is identical to the GC-FID-ECD system (see Section 10.3).

10.3.4.4 Table 8 outlines typical retention times (minutes) for selected organics using the GC-FID-ECD-PID analytical system.

10.4 Analytical Procedures

10.4.1 Canister Receipt

10.4.1.1 The overall condition of each sample canister is observed. Each canister should be received with an attached sample identification tag.

10.4.1.2 Each canister is recorded in the dedicated laboratory logbook. Also noted on the identification tag are date received and initials of recipient.

10.4.1.3 The pressure of the canister is checked by attaching a pressure gauge to the canister inlet. The canister valve is opened briefly and the pressure (kPa, psig) is recorded. [Note: If pressure is <83 kPa (<12 psig), the user may wish to pressurize the canisters, as an option, with zero grade nitrogen up to 137 kPa (20 psig) to ensure that enough sample is available for analysis. However, pressurizing the canister can introduce additional error, increase the minimum detection limit (MDL), and is time consuming. The user should weigh these limitations as part of his program objectives before pressurizing.] Final cylinder pressure is recorded on canister sampling field data sheet (see Figure 10).

10.4.1.4 If the canister pressure is increased, a dilution factor (DF) is calculated and recorded on the sampling data sheet.

$$DF = \frac{Y_a}{X_a}$$

where:

X_a = canister pressure (kPa, psia) absolute before dilution.

Y_a = canister pressure (kPa, psia) absolute after dilution.

After sample analysis, detected VOC concentrations are multiplied by the dilution factor to determine concentration in the sampled air.

10.4.2 GC-MS-SCAN Analysis (With Optional FID System)

10.4.2.1 The analytical system should be properly assembled, humid zero air certified (see Section 12.3), operated (see Table 3), and calibrated for accurate VOC determination.

10.4.2.2 The mass flow controllers are checked and adjusted to provide correct flow rates for the system.

10.4.2.3 The sample canister is connected to the inlet of the GC-MS-SCAN (with optional FID) analytical system. For pressurized samples, a mass flow controller is placed on the canister and the canister valve is opened and the canister flow is vented past a tee inlet to the analytical system at a flow of 75 cm^3/min so that 40 cm^3/min is pulled through the Nafion® dryer to the six-port chromatographic valve. [Note: Flow rate is not as important as acquiring sufficient sample volume.] Sub-ambient pressure samples are connected directly to the inlet.

10.4.2.4 The GC oven and cryogenic trap (inject position) are cooled to their set points of -50°C and -160°C, respectively.

10.4.2.5 As soon as the cryogenic trap reaches its lower set point of -160°C, the six-port chromatographic valve is turned to its fill position to initiate sample collection.

10.4.2.6 A ten minute collection period of canister sample is utilized. [Note: 40 cm^3/min x 10 min = 400 cm^3 sampled canister contents.]

10.4.2.7 After the sample is preconcentrated in the cryogenic trap, the GC sampling valve is cycled to the inject position and the cryogenic trap is heated. The trapped analytes are thermally desorbed onto the head of the OV-1 capillary column (0.31 mm I.D. x 50 m length). The GC oven is programmed to start at -50°C and after 2 min to heat to 150°C at a rate of 8°C per minute.

10.4.2.8 Upon sample injection onto the column, the MS is signaled by the computer to scan the eluting carrier gas from 18 to 250 amu, resulting in a 1.5 Hz repetition rate. This corresponds to about 6 scans per eluting chromatographic peak.

10.4.2.9 Primary identification is based upon retention time and relative abundance of eluting ions as compared to the spectral library stored on the hard disk of the GC-MS data computer.

10.4.2.10 The concentration (ppbv) is calculated using the previously established response factors (see Section 10.2.3.2), as illustrated in Table 5. [Note: If the canister is diluted before analysis, an appropriate multiplier is applied to correct for the volume dilution of the canister (Section 10.4.1.4).]

10.4.2.11 The optional FID trace allows the analyst to record the progress of the analysis.

10.4.3 GC-MS-SIM Analysis (With Optional FID System)

10.4.3.1 When the MS is placed in the SIM mode of operation, the MS monitors only preselected ions, rather than scanning all masses continuously between two mass limits.

10.4.3.2 As a result, increased sensitivity and improved quantitative analysis can be achieved.

10.4.3.3 Similar to the GC-MS-SCAN configuration, the GC-MS-SIM analysis is based on a combination of retention times and relative abundances of selected ions (see Table 2 and Table 5). These qualifiers are stored on the hard disk of the GC-MS computer and are applied for identification of each chromatographic peak. Once the GC-MS-SIM has identified the peak, a calibration response factor is used to determine the analyte's concentration.

10.4.3.4 The individual analyses are handled in three phases: data acquisition, data reduction, and data reporting. The data acquisition software is set in the SIM mode, where specific compound fragments are monitored by the MS at specific times in the analytical run. Data reduction is coordinated by the postprocessing macro program that is automatically accessed after data acquisition is completed at the end of the GC run. Resulting ion profiles are extracted, peaks are identified and integrated, and an internal integration report is generated by the program. A reconstructed ion chromatogram for hardcopy reference is prepared by the program and various parameters of interest such as time, date, and integration constants are printed. At the completion of the macro program, the data reporting software is accessed. The appropriate calibration table (see Table 9) is retrieved by the data reporting program from the computer's hard disk storage and the proper retention time and response factor parameters are applied to the macro program's integration file. With reference to certain pre-set acceptance criteria, peaks are automatically identified and quantified and a final summary report is prepared, as illustrated in Table 10.

10.4.4 GC-FID-ECD Analysis (With Optional PID System)

10.4.4.1 The analytical system should be properly assembled, humid zero air certified (see Section 12.2) and calibrated through a dynamic standard calibration procedure (see Section 10.3.2). The FID detector is lit and allowed to stabilize.

10.4.4.2 Sixty-four minutes are required for each sample analysis - 15 min for system initialization, 14 min for sample collection, 30 min for analysis, and 5 min for post-time, during which a report is printed. [Note: This may vary depending upon system configuration and programming.]

10.4.4.3 The helium and sample mass flow controllers are checked and adjusted to provide correct flow rates for the system. Helium is used to purge residual air from the trap at the end of the sampling phase and to carry the revolatilized VOCs from the trap onto the GC column and into the FID-ECD. The hydrogen, burner air, and nitrogen flow rates should also be checked. The cryogenic trap is connected and verified to be operating properly while flowing cryogen through the system.

10.4.4.4 The sample canister is connected to the inlet of the GC-FID-ECD analytical system. The canister valve is opened and the canister flow is vented past a tee inlet to the analytical system at 75 cm^3/min using a 0-500 cm^3/min Tylan mass flow controller. During analysis, 40 cm^3/min of sample gas is pulled through the six-port chromatographic valve and routed through the trap at the appropriate time while the extra sample is vented. The VOCs are condensed in the trap while the excess flow is exhausted through an exhaust vent, which assures that the sample air flowing through the trap is at atmospheric pressure.

10.4.4.5 The six-port valve is switched to the inject position and the canister valve is closed.

10.4.4.6 The electronic integrator is started.

10.4.4.7 After the sample is preconcentrated on the trap, the trap is heated and the VOCs are thermally desorbed onto the head of the capillary column. Since the column is at -50°C, the VOCs are cryofocussed on the column. Then, the oven temperature (programmed) increases and the VOCs elute from the column to the parallel FID-ECD assembly.

10.4.4.8 The peaks eluting from the detectors are identified by retention time (see Table 7 and Table 8), while peak areas are recorded in area counts. Figures 15 and 16 illustrate typical response of the FID and ECD, respectively, for the forty (40) targeted VOCs. [Note: Refer to Table 7 for peak number and identification.]

10.4.4.9 The response factors (see Section 10.3.3.1) are multiplied by the area counts for each peak to calculate ppbv estimates for the unknown sample. If the canister is diluted before analysis, an appropriate dilution multiplier (DF) is applied to correct for the volume dilution of the canister (see Section 10.4.1.4).

10.4.4.10 Depending on the number of canisters to be analyzed, each canister is analyzed twice and the final concentrations for each analyte are the averages of the two analyses.

10.4.4.11 However, if the GC-FID-ECD analytical system discovers unexpected peaks which need further identification and attention or overlapping peaks are discovered, eliminating possible quantitation, the sample should then be subjected to a GC-MS-SCAN for positive identification and quantitation.

11. Cleaning and Certification Program

11.1 Canister Cleaning and Certification

11.1.1 All canisters must be clean and free of any contaminants before sample collection.

11.1.2 All canisters are leak tested by pressurizing them to approximately 206 kPa (30 psig) with zero air. [Note: The canister cleaning system in Figure 7 can be used for this task.] The initial pressure is measured, the canister valve is closed, and the final pressure is checked after 24 hours. If leak tight, the pressure should not vary more than ± 13.8 kPa (± 2 psig) over the 24 hour period.

11.1.3 A canister cleaning system may be assembled as illustrated in Figure 7. Cryogen is added to both the vacuum pump and zero air supply traps. The canister(s) are connected to the manifold. The vent shut-off valve and the canister valve(s) are opened to release any remaining pressure in the canister(s). The vacuum pump is started and the vent shut-off valve is then closed and the vacuum shut-off valve is opened. The canister(s) are evacuated to < 0.05 mm Hg (for at least one hour). [Note: On a daily basis or more often if necessary, the cryogenic traps should be purged with zero air to remove any trapped water from previous canister cleaning cycles.]

11.1.4 The vacuum and vacuum/pressure gauge shut-off valves are closed and the zero air shut-off valve is opened to pressurize the canister(s) with humid zero air to approximately 206 kPa (30 psig). If a zero gas generator system is used, the flow rate may need to be limited to maintain the zero air quality.

11.1.5 The zero shut-off valve is closed and the canister(s) is allowed to vent down to atmospheric pressure through the vent shut-off valve. The vent shut-off valve is closed. Steps 11.1.3 through 11.1.5 are repeated two additional times for a total of three (3) evacuation/pressurization cycles for each set of canisters.

11.1.6 At the end of the evacuation/pressurization cycle, the canister is pressurized to 206 kPa (30 psig) with humid zero air. The canister is then analyzed by a GC-MS or GC-FID-ECD analytical system. Any canister that has not tested clean (compared to direct analysis of humidified zero air of less than 0.2 ppbv of targeted VOCs) should not be used. As a "blank" check of the canister(s) and cleanup procedure, the final humid zero air fill of 100% of the canisters is analyzed until the cleanup system and canisters are proven reliable (less than 0.2 ppbv of targets VOCs). The check can then be reduced to a lower percentage of canisters.

11.1.7 The canister is reattached to the cleaning manifold and is then reevacuated to <0.05 mm Hg and remains in this condition until used. The canister valve is closed. The canister is removed from the cleaning system and the canister connection is capped with a stainless steel fitting.

The canister is now ready for collection of an air sample. An identification tag is attached to the neck of each canister for field notes and chain-of-custody purposes.

11.1.8 As an option to the humid zero air cleaning procedures, the canisters could be heated in an isothermal oven to 100°C during Section 11.1.3 to ensure that lower molecular weight compounds (C_2-C_8) are not retained on the walls of the canister. [Note: For sampling heavier, more complex VOC mixtures, the canisters should be heated to 250°C during Section 11.1.3.7.] Once heated, the canisters are evacuated to 0.05 mm Hg. At the end of the heated/evacuated cycle, the canisters are pressurized with humid zero air and analyzed by the GC-FID-ECD system. Any canister that has not tested clean (less than 0.2 ppbv of targeted compounds) should not be used. Once tested clean, the canisters are reevacuated to 0.05 mm Hg and remain in the evacuated state until used.

11.2 Sampling System Cleaning and Certification

11.2.1 Cleaning Sampling System Components

11.2.1.1 Sample components are disassembled and cleaned before the sampler is assembled. Nonmetallic parts are rinsed with HPLC grade deionized water and dried in a vacuum oven at 50°C. Typically, stainless steel parts and fittings are cleaned by placing them in a beaker of methanol in an ultrasonic bath for 15 minutes. This procedure is repeated with hexane as the solvent.

11.2.1.2 The parts are then rinsed with HPLC grade deionized water and dried in a vacuum oven at 100°C for 12 to 24 hours.

11.2.1.3 Once the sampler is assembled, the entire system is purged with humid zero air for 24 hours.

11.2.2 Humid Zero Air Certification

[Note: In the following sections, "certification" is defined as evaluating the sampling system with humid zero air and humid calibration gases that pass through all active components of the sampling system. The system is "certified" if no significant additions or deletions (less than 0.2 ppbv of targeted compounds) have occurred when challenged with the test gas stream.]

11.2.2.1 The cleanliness of the sampling system is determined by testing the sampler with humid zero air without an evacuated gas cylinder, as follows.

11.2.2.2 The calibration system and manifold are assembled, as illustrated in Figure 8. The sampler (without an evacuated gas cylinder) is connected to the manifold and the zero air cylinder activated to generate a humid gas stream (2 L/min) to the calibration manifold [see Figure 8(b)].

11.2.2.3 The humid zero gas stream passes through the calibration manifold, through the sampling system (without an evacuated canister) to a GC-FID-ECD analytical system at 75 cm^3/min so that 40 cm^3/min is pulled through the six-port valve and routed through the cryogenic trap (see Section 10.2.2.1) at the appropriate time while the extra sample is vented. [Note: The exit of the sampling system (without the canister) replaces the canister in Figure 4.] After the sample (400 mL) is preconcentrated on the trap, the trap is heated and the VOCs are thermally desorbed onto the head of the capillary column. Since the column is at -50°C, the VOCs are cryofocussed on the column. Then, the oven temperature (programmed) increases and the VOCs begin to elute and are detected by a GC-MS (see Section 10.2) or the GC-FID-ECD (see Section 10.3). The analytical system should not detect greater than 0.2 ppbv of targeted VOCs in order for the sampling system to pass the humid zero air certification test. Chromatograms of a certified sampler and contaminated sampler are illustrated in Figures 17(a) and (b), respectively. If the sampler passes the humid zero air test, it is then tested with humid calibration gas standards containing selected VOCs at concentration levels expected in field sampling (e.g., 0.5 to 2 ppbv) as outlined in Section 11.2.3.

11.2.3 Sampler System Certification with Humid Calibration Gas Standards

11.2.3.1 Assemble the dynamic calibration system and manifold as illustrated in Figure 8.

11.2.3.2 Verify that the calibration system is clean (less than 0.2 ppbv of targeted compounds) by sampling a humidified gas stream, without gas calibration standards, with a previously certified clean canister (see Section 12.1).

11.2.3.3 The assembled dynamic calibration system is certified clean if less than 0.2 ppbv of targeted compounds are found.

11.2.3.4 For generating the humidified calibration standards, the calibration gas cylinder(s) (see Section 8.2) containing nominal concentrations of 10 ppmv in nitrogen of selected VOCs, are attached to the calibration system, as outlined in Section 10.2.3.1. The gas cylinders are opened and the gas mixtures are passed through 0 to 10 cm^3/min certified mass flow controllers to generate ppb levels of calibration standards.

11.2.3.5 After the appropriate equilibrium period, attach the sampling system (containing a certified evacuated canister) to the manifold, as illustrated in Figure 8(a).

11.2.3.6 Sample the dynamic calibration gas stream with the sampling system according to Section 9.2.1. [Note: To conserve generated calibration gas, bypass the canister sampling system manifold and attach the sampling system to the calibration gas stream at the inlet of the in-line filter of the sampling system so the flow will be less than 500 cm^3/min.]

11.2.3.7 Concurrent with the sampling system operation, realtime monitoring of the calibration gas stream is accomplished by the on-line GC-MS or GC-multidetector analytical system [Figure 8(b)] to provide reference concentrations of generated VOCs.

11.2.3.8 At the end of the sampling period (normally same time period used for anticipated sampling), the sampling system canister is analyzed and compared to the reference GC-MS or GC-multidetector analytical system to determine if the concentration of the targeted VOCs was increased or decreased by the sampling system.

11.2.3.9 A recovery of between 90% and 110% is expected for all targeted VOCs.

12. Performance Criteria and Quality Assurance

12.1 Standard Operating Procedures (SOPs)

12.1.1 SOPs should be generated in each laboratory describing and documenting the following activities: (1) assembly, calibration, leak check, and operation of specific sampling systems and equipment used; (2) preparation, storage, shipment, and handling of samples; (3) assembly, leak-check, calibration, and operation of the analytical system, addressing the specific equipment used; (4) canister storage and cleaning; and (5) all aspects of data recording and processing, including lists of computer hardware and software used.

12.1.2 Specific stepwise instructions should be provided in the SOPs and should be readily available to and understood by the laboratory personnel conducting the work.

12.2 Method Relative Accuracy and Linearity

12.2.1 Accuracy can be determined by injecting VOC standards (see Section 8.2) from an audit cylinder into a sampler. The contents are then analyzed for the components contained in the audit canister. Percent relative accuracy is calculated:

$$\% \text{ Relative Accuracy} = \frac{Y - X}{X} \times 100$$

Where: Y = Concentration of the targeted compound recovered from sampler.

X = Concentration of VOC targeted compound in the NBS-SRM or EPA-CRM audit cylinders.

12.2.2 If the relative accuracy does not fall between 90 and and 110 percent, the field sampler should be removed from use, cleaned, and recertified according to initial certification procedures outlined in Section 11.2.2 and Section 11.2.3. Historically, concentrations of carbon tetrachloride, tetrachloroethylene, and hexachlorobutadiene have sometimes been detected at lower concentrations when using parallel ECD and FID detectors. When these three compounds are present at concentrations close to calibration levels, both detectors usually agree on the reported concentrations. At concentrations below 4 ppbv, there is a problem with nonlinearity of the ECD. Plots of concentration versus peak area for calibration compounds detected by the ECD have shown that the curves are nonlinear for carbon tetrachloride, tetrachloroethylene, and hexachlorobutadiene, as illustrated in Figures 18(a) through 18(c). Other targeted ECD and FID compounds scaled linearly for the range 0 to 8 ppbv, as shown for chloroform in Figure 18(d). For compounds that are not linear over the calibration range, area counts generally roll off between 3 and 4 ppbv. To correct for the nonlinearity of these compounds, an additional calibration step is performed. An evacuated stainless steel canister is pressurized with calibration gas at a nominal concentration of 8 ppbv. The sample is then diluted to approximately 3.5 ppbv with zero air and analyzed. The instrument response factor (ppbv/area) of the ECD for each of the three compounds is calculated for the 3.5 ppbv sample. Then, both the 3.5 ppbv and the 8 ppbv response factors are entered into the ECD calibration table. The software for the Hewlett-Packard 5880 level 4 GC is designed to accommodate multilevel calibration entries, so the correct response factors are automatically calculated for concentrations in this range.

12.3 Method Modification

12.3.1 Sampling

12.3.1.1 The sampling system for pressurized canister sampling could be modified to use a lighter, more compact pump. The pump currently being used weighs about 16 kilograms (35 lbs). Commercially available pumps that could be used as alternatives to the prescribed sampler pump are described below. Metal Bellows MB-41 pump: These pumps are cleaned at the factory; however, some precaution should be taken with the circular (4.8 cm diameter) Teflon® and stainless steel part directly under the flange. It is often dirty when received and should be cleaned before use. This part is cleaned by removing it from the pump, manually cleaning with deionized water, and placing in a vacuum oven at 100°C for at least 12 hours. Exposed parts of the pump head are also cleaned with swabs and allowed to air dry. These pumps have proven to be very reliable; however, they are only useful up to an outlet pressure of about 137 kPa (20 psig). Neuberger Pump: Viton gaskets or seals must be specified with this pump. The "factory direct" pump is received contaminated and leaky. The pump is cleaned by disassembling the pump head (which consists of three stainless steel parts and two gaskets), cleaning the gaskets with deionized water and drying in a vacuum oven, and remachining (or manually lapping) the sealing surfaces of the stainless steel parts. The stainless steel parts are then cleaned with methanol, hexane, deionized water and heated in a vacuum oven. The cause for most of the problems with this pump has been scratches on the metal parts of the pump head. Once this rework procedure is performed, the pump is considered clean and can be used up to about 240 kPa (35 psig) output pressure. This pump is utilized in the sampling system illustrated in Figure 3.

12.3.1.2 Urban Air Toxics Sampler

The sampling system described in this method can be modified like the sampler in EPA's FY-88 Urban Air Toxics Pollutant Program. This particular sampler is described in Appendix C (see Figure 19).

12.3.2 Analysis

12.3.2.1 Inlet tubing from the calibration manifold could be heated to 50°C (same temperature as the calibration manifold) to prevent condensation on the internal walls of the system.

12.3.2.2 The analytical strategy for Method TO-14 involves positive identification and quantitation by GC-MS-SCAN-SIM mode of operation with optional FID. This is a highly specific and sensitive detection technique. Because a specific detector system (GC-MS-SCAN-SIM) is more complicated and expensive than the use of non-specific detectors

(GC-FID-ECD-PID), the analyst may want to perform a screening analysis and preliminary quantitation of VOC species in the sample, including any polar compounds, by utilizing the GC-multidetector (GC-FID-ECD-PID) analytical system prior to GC-MS analysis. This system can be used for approximate quantitation. The GC-FID-ECD-PID provides a "snapshot" of the constituents in the sample, allowing the analyst to determine:

- Extent of misidentification due to overlapping peaks,
- Whether the constituents are within the calibration range of the anticipated GC-MS-SCAN-SIM analysis or does the sample require further dilution, and
- Are there unexpected peaks which need further identification through GC-MS-SCAN or are there peaks of interest needing attention?

If unusual peaks are observed from the GC-FID-ECD-PID system, the analyst then performs a GC-MS-SCAN analysis. The GC-MS-SCAN will provide positive identification of suspect peaks from the GC-FID-ECD-PID system. If no unusual peaks are identified and only a select number of VOCs are of concern, the analyst can then proceed to GC-MS-SIM. The GC-MS-SIM is used for final quantitation of selected VOCs. Polar compounds, however, cannot be identified by the GC-MS-SIM due to the use of a Nafion® dryer to remove water from the sample prior to analysis. The dryer removes polar compounds along with the water. The analyst often has to make this decision incorporating project objectives, detection limits, equipment availability, cost and personnel capability in developing an analytical strategy. Figure 20 outlines the use of the GC-FID-ECD-PID as a "screening" approach, with the GC-MS-SCAN-SIM for final identification and quantitation.

12.4 Method Safety

This procedure may involve hazardous materials, operations, and equipment. This method does not purport to address all of the safety problems associated with its use. It is the user's responsibility to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to the implementation of this procedure. This should be part of the user's SOP manual.

12.5 Quality Assurance (See Figure 21)

12.5.1 Sampling System

12.5.1.1 Section 9.2 suggests that a portable GC system be used as a "screening analysis" prior to locating fixed-site samplers (pressurized or subatmospheric).

12.5.1.2 Section 9.2 requires pre and post-sampling measurements with a certified mass flow controller for flow verification of sampling system.

12.5.1.3 Section 11.1 requires all canisters to be pressure tested to 207 kPa ± 14 kPa (30 psig ± 2 psig) over a period of 24 hours.

12.5.1.4 Section 11.1 requires that all canisters be certified clean (containing less than 0.2 ppbv of targeted VOCs) through a humid zero air certification program.

12.5.1.5 Section 11.2.2 requires all field sampling systems to be certified initially clean (containing less than 0.2 ppbv of targeted VOCs) through a humid zero air certification program.

12.5.1.6 Section 11.2.3 requires all field sampling systems to pass an initial humidified calibration gas certification [at VOC concentration levels expected in the field (e.g., 0.5 to 2 ppbv)] with a percent recovery of greater than 90.

12.5.2 GC-MS-SCAN-SIM System Performance Criteria

12.5.2.1 Section 10.2.1 requires the GC-MS analytical system to be certified clean (less than 0.2

ppbv of targeted VOCs) prior to sample analysis, through a humid zero air certification.

12.5.2.2 Section 10.2.2 requires the daily tuning of the GC-MS with 4-bromofluorobenzene (4-BFB) and that it meet the key ions and ion abundance critera (10%) outlined in Table 5.

12.5.2.3 Section 10.2.3 requires both an initial multipoint humid static calibration (three levels plus humid zero air) and a daily calibration (one point) of the GC-MS analytical system.

12.5.3 GC-Multidetector System Performance Criteria

12.5.3.1 Section 10.3.1 requires the GC-FID-ECD analytical system, prior to analysis, to be certified clean (less than 0.2 ppbv of targeted VOCs) through a humid zero air certification.

12.5.3.2 Section 10.3.2 requires that the GC-FID-ECD analytical system establish retention time windows for each analyte prior to sample analysis, when a new GC column is installed, or major components of the GC system altered since the previous determination.

12.5.3.3 Section 8.2 requires that all calibration gases be traceable to a National Bureau of Standards (NBS) Standard Reference Material (SRM) or to a NBS/EPA approved Certified Reference Material (CRM).

12.5.3.4 Section 10.3.2 requires that the retention time window be established throughout the course of a 72-hr analytical period.

12.5.3.5 Section 10.3.3 requires both an initial multipoint calibration (three levels plus humid zero air) and a daily calibration (one point) of the GC-FID-ECD analytical system with zero gas dilution of NBS traceable or NBS/EPA CRMs gases. [Note: Gas cylinders of VOCs at the ppm and ppb level are available for audits from the USEPA, Environmental Monitoring Systems

Laboratory, Quality Assurance Division, MD-77B, Research Triangle Park, NC 27711, (919)541-4531. Appendix A outlines five groups of audit gas cylinders available from USEPA.]

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The determination of volatile and some semi-volatile organic compounds in ambient air is a complex task, primarily because of the wide variety of compounds of interest and the lack of standardized sampling and analytical procedures. While there are numerous procedures for sampling and analyzing VOCs/SVOCs in ambient air, this method draws upon the best aspects of each one and combines them into a standardized methodology. To that end, the following individuals contributed to the research, documentation and peer review of this manuscript.

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TABLE 1. VOLATILE ORGANIC COMPOUND DATA SHEET

COMPOUND (SYNONYM)	FORMULA	MOLECULAR WEIGHT	BOILING POINT (°C)	MELTING POINT (°C)	CAS NUMBER
Freon 12 (Dichlorodifluoromethane)	Cl_2CF_2	120.91	-29.8	-158.0	
Methyl chloride (Chloromethane)	CH_3Cl	50.49	-24.2	-97.1	74-87-3
Freon 114 (1,2-Dichloro-1,1,2,2-tetrafluoroethane)	$ClCF_2CClF_2$	170.93	4.1	-94.0	
Vinyl chloride (Chloroethylene)	$CH_2{=}CHCl$	62.50	-13.4	-1538.0	75-01-4
Methyl bromide (Bromomethane)	CH_3Br	94.94	3.6	-93.6	74-83-9
Ethyl chloride (Chloroethane)	CH_3CH_2Cl	64.52	12.3	-136.4	75-00-3
Freon 11 (Trichlorofluoromethane)	CCl_3F	137.38	23.7	-111.0	
Vinylidene chloride (1,1-Dichloroethene)	$C_2H_2Cl_2$	96.95	31.7	-122.5	75-35-4
Dichloromethane (Methylene chloride)	CH_2Cl_2	84.94	39.8	-95.1	75-09-2
Freon 113 (1,1,2-Trichloro-1,2,2-trifluoroethane)	CF_2ClCCl_2F	187.38	47.7	-36.4	
1,1-Dichloroethane (Ethylidene chloride)	CH_3CHCl_2	98.96	57.3	-97.0	74-34-3
cis-1,2-Dichloroethylene	$CHCl{=}CHCl$	96.94	60.3	-80.5	
Chloroform (Trichloromethane)	$CHCl_3$	119.38	61.7	-63.5	67-66-3
1,2-Dichloroethane (Ethylene dichloride)	$ClCH_2CH_2Cl$	98.96	83.5	-35.3	107-06-2
Methyl chloroform (1,1,1-Trichloroethane)	CH_3CCl_3	133.41	74.1	-30.4	71-55-6
Benzene (Cyclohexatriene)	C_6H_6	78.12	80.1	5.5	71-43-2
Carbon tetrachloride (Tetrachloromethane)	CCl_4	153.82	76.5	-23.0	56-23-5
1,2-Dichloropropane (Propylene dichloride)	$CH_3CHClCH_2Cl$	112.99	96.4	-100.4	78-87-5
Trichloroethylene (Trichloroethene)	$ClCH{=}CCl_2$	131.29	87	-73.0	79-01-6
cis-1,3-Dichloropropene (cis-1,3-dichloropropylene)	$CH_3CCl{=}CHCl$	110.97	76		

TABLE 1. VOLATILE ORGANIC COMPOUND DATA SHEET (cont.)

COMPOUND (SYNONYM)	FORMULA	MOLECULAR WEIGHT	BOILING POINT (°C)	MELTING POINT (°C)	CAS NUMBER
trans-1,3-Dichloropropene (cis-1,3-Dichloropropylene)	$ClCH_2CH=CHCl$	110.97	112.0		
1,1,2-Trichloroethane (Vinyl trichloride)	$CH_2ClCHCl_2$	133.41	113.8	-36.5	79-00-5
Toluene (Methyl benzene)	$C_6H_5CH_3$	92.15	110.6	-95.0	108-88-3
1,2-Dibromoethane (Ethylene dibromide)	$BrCH_2CH_2Br$	187.88	131.3	9.8	106-93-4
Tetrachloroethylene (Perchloroethylene)	$Cl_2C=CCl_2$	165.83	121.1	-19.0	127-18-4
Chlorobenzene (Phenyl chloride)	C_6H_5Cl	112.56	132.0	-45.6	108-90-7
Ethylbenzene	$C_6H_5C_2H_5$	106.17	136.2	-95.0	100-41-4
m-Xylene (1,3-Dimethylbenzene)	$1,3\text{-}(CH_3)_2C_6H_4$	106.17	139.1	-47.9	
p-Xylene (1,4-Dimethylxylene)	$1,4\text{-}(CH_3)_2C_6H_4$	106.17	138.3	13.3	
Styrene (Vinyl benzene)	$C_6H_5CH=CH_2$	104.16	145.2	-30.6	100-42-5
1,1,2,2-Tetrachloroethane	$CHCl_2CHCl_2$	167.85	146.2	-36.0	79-34-5
o-Xylene (1,2-Dimethylbenzene)	$1,2\text{-}(CH_3)_2C_6H_4$	106.17	144.4	-25.2	
1,3,5-Trimethylbenzene (Mesitylene)	$1,3,5\text{-}(CH_3)_3C_6H_6$	120.20	164.7	-44.7	108-67-8
1,2,4-Trimethylbenzene (Pseudocumene)	$1,2,4\text{-}(CH_3)_3C_6H_6$	120.20	169.3	-43.8	95-63-6
m-Dichlorobenzene (1,3-Dichlorobenzene)	$1,3\text{-}Cl_2C_6H_4$	147.01	173.0	-24.7	541-73-1
Benzyl chloride (α-Chlorotoluene)	$C_6H_5CH_2Cl$	126.59	179.3	-39.0	100-44-7
o-Dichlorobenzene (1,2-Dichlorobenzene)	$1,2\text{-}Cl_2C_6H_4$	147.01	180.5	-17.0	95-50-1
p-Dichlorobenzene (1,4-Dichlorobenzene)	$1,4\text{-}Cl_2C_6H_4$	147.01	174.0	53.1	106-46-7
1,2,4-Trichlorobenzene	$1,2,4\text{-}Cl_3C_6H_3$	181.45	213.5	17.0	120-82-1
Hexachlorobutadiene (1,1,2,3,4,4-Hexachloro-1,3-butadiene)					

TABLE 2. ION/ABUNDANCE AND EXPECTED RETENTION TIME FOR SELECTED VOCs ANALYZED BY GC-MS-SIM

Compound	Ion/Abundance (amu/% base peak)	Expected Retention Time (min)
Freon 12 (Dichlorodifluoromethane)	85/100	5.01
	87/ 31	
Methyl chloride (Chloromethane)	50/100	5.69
	52/ 34	
Freon 114 (1,2-Dichloro-1,1,2,2-tetrafluoroethane)	85/100	6.55
	135/ 56	
	87/ 33	
Vinyl chloride (Chloroethene)	62/100	6.71
	27/125	
	64/ 32	
Methyl bromide (Bromomethane)	94/100	7.83
	96/ 85	
Ethyl chloride (Chloroethane)	64/100	8.43
	29/140	
	27/140	
Freon 11 (Trichlorofluoromethane)	101/100	9.97
	103/ 67	
Vinylidene chloride (1,1-Dichloroethylene)	61/100	10.93
	96/ 55	
	63/ 31	
Dichloromethane (Methylene chloride)	49/100	11.21
	84/ 65	
	86/ 45	
Freon 113 (1,1,2-Trichloro-1,2,2-trifluoroethane)	151/100	11.60
	101/140	
	103/ 90	
1,1-Dichloroethane (Ethylidene dichloride)	63/100	12.50
	27/ 64	
	65/ 33	
cis-1,2-Dichloroethylene	61/100	13.40
	96/ 60	
	98/ 44	
Chloroform (Trichloromethane)	83/100	13.75
	85/ 65	
	47/ 35	
1,2-Dichloroethane (Ethylene dichloride)	62/100	14.39
	27/ 70	
	64/ 31	
Methyl chloroform (1,1,1-Trichloroethane)	97/100	14.62
	99/ 64	
	61/ 61	
Benzene (Cyclohexatriene)	78/100	15.04
	77/ 25	
	50/ 35	
Carbon tetrachloride (Tetrachloromethane)	117/100	15.18
	119/ 97	

(continued)

TABLE 2. ION/ABUNDANCE AND EXPECTED RETENTION TIME FOR SELECTED VOCs ANALYZED BY GC-MS-SIM (cont.)

Compound	Ion/Abundance (amu/% base peak)	Estimated Retention Time (min)
1,2-Dichloropropane (Propylene dichloride)	63/100 41/ 90 62/ 70	15.83
Trichloroethylene (Trichloroethene)	130/100 132/ 92 95/ 87	16.10
cis-1,3-Dichloropropene	75/100 39/ 70 77/ 30	16.96
trans-1,3-Dichloropropene (1,3 dichloro-1-propene)	75/100 39/ 70 77/ 30	17.49
1,1,2-Trichloroethane (Vinyl trichloride)	97/100 83/ 90 61/ 82	17.61
Toluene (Methyl benzene)	91/100 92/ 57	17.86
1,2-Dibromoethane (Ethylene dibromide)	107/100 109/ 96 27/115	18.48
Tetrachloroethylene (Perchloroethylene)	166/100 164/ 74 131/ 60	19.01
Chlorobenzene (Benzene chloride)	112/100 77/ 62 114/ 32	19.73
Ethylbenzene	91/100 106/ 28	20.20
m,p-Xylene(1,3/1,4-dimethylbenzene)	91/100 106/ 40	20.41
Styrene (Vinyl benzene)	104/100 78/ 60 103/ 49	20.81
1,1,2,2-Tetrachloroethane (Tetrachloroethane)	83/100 85/ 64	20.92
o-Xylene (1,2-Dimethylbenzene)	91/100 106/ 40	20.92
4-Ethyltoluene	105/100 120/ 29	22.53
1,3,5-Trimethylbenzene (Mesitylene)	105/100 120/ 42	22.65
1,2,4-Trimethylbenzene (Pseudocumene)	105/100 120/ 42	23.18
m-Dichlorobenzene (1,3-Dichlorobenzene)	146/100 148/ 65 111/ 40	23.31

(continued)

TABLE 2. ION/ABUNDANCE AND EXPECTED RETENTION TIME FOR SELECTED VOCs ANALYZED BY GC-MS-SIM (cont.)

Compound	Ion/Abundance (amu/% base peak)	Expected Retention Time (min)
Benzyl chloride (α-Chlorotoluene)	91/100	23.32
	126/ 26	
p-Dichlorobenzene (1,4-Dichlorobenzene)	146/100	23.41
	148/ 65	
	111/ 40	
o-Dichlorobenzene (1,2-Dichlorobenzene)	146/100	23.88
	148/ 65	
	111/ 40	
1,2,4-Trichlorobenzene	180/100	26.71
	182/ 98	
	184/ 30	
Hexachlorobutadiene (1,1,2,3,4,4 Hexachloro-1,3-butadiene)	225/100	27.68
	227/ 66	
	223/ 60	

TABLE 3. GENERAL GC AND MS OPERATING CONDITIONS

Chromatography	
Column	Hewlett-Packard OV-1 crosslinked methyl silicone (50 m x 0.31-mm I.D., 17 um film thickness), or equivalent
Carrier Gas	Helium (2.0 cm^3/min at 250°C)
Injection Volume	Constant (1-3 uL)
Injection Mode	Splitless
Temperature Program	
Initial Column Temperature	-50°C
Initial Hold Time	2 min
Program	8°C/min to 150°C
Final Hold Time	15 min
Mass Spectrometer	
Mass Range	18 to 250 amu
Scan Time	1 sec/scan
EI Condition	70 eV
Mass Scan	Follow manufacturer's instruction for selecting mass selective detector (MS) and selected ion monitoring (SIM) mode
Detector Mode	Multiple ion detection
FID System (Optional)	
Hydrogen Flow	30 cm^3/minute
Carrier Flow	30 cm^3/minute
Burner Air	400 cm^3/minute

TABLE 4. 4-BROMOFLUOROBENZENE KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	Base Peak, 100% Relative Abundance
96	5 to 9% of mass 95
173	<2% of mass 174
174	>50% of mass 95
175	5 to 9% of mass 174
176	>95% but< 101% of mass 174
177	5 to 9% of mass 176

TABLE 5. RESPONSE FACTORS (ppbv/area count) AND EXPECTED RETENTION TIME FOR GC-MS-SIM ANALYTICAL CONFIGURATION

Compounds	Response Factor (ppbv/area count)	Expected Retention Time (minutes)
Freon 12	0.6705	5.01
Methyl chloride	4.093	5.64
Freon 114	0.4928	6.55
Vinyl chloride	2.343	6.71
Methyl bromide	2.647	7.83
Ethyl chloride	2.954	8.43
Freon 11	0.5145	9.87
Vinylidene chloride	1.037	10.93
Dichloromethane	2.255	11.21
Trichlorotrifluoroethane	0.9031	11.60
1,1-Dichloroethane	1.273	12.50
cis-1,2-Dichloroethylene	1.363	13.40
Chloroform	0.7911	13.75
1,2-Dichloroethane	1.017	14.39
Methyl chloroform	0.7078	14.62
Benzene	1.236	15.04
Carbon tetrachloride	0.5880	15.18
1,2-Dichloropropane	2.400	15.83
Trichloroethylene	1.383	16.10
cis-1,3-Dichloropropene	1.877	16.96
trans-1,3-Dichloropropene	1.338	17.49
1,1,2-Trichloroethane	1.891	17.61
Toluene	0.9406	17.86
1,2-Dibromoethane (EDB)	0.8662	18.48
Tetrachloroethylene	0.7357	19.01
Chlorobenzene	0.8558	19.73
Ethylbenzene	0.6243	20.20
m,p-Xylene	0.7367	20.41
Styrene	1.888	20.80
1,1,2,2-Tetrachloroethane	1.035	20.92
o-Xylene	0.7498	20.92
4-Ethyltoluene	0.6181	22.53
1,3,5-Trimethylbenzene	0.7088	22.65
1,2,4-Trimethylbenzene	0.7536	23.18
m-Dichlorobenzene	0.9643	23.31
Benzyl chloride	1.420	23.32
p-Dichlorobenzene	0.8912	23.41
o-Dichlorobenzene	1.004	23.88
1,2,4-Trichlorobenzene	2.150	26.71
Hexachlorobutadiene	0.4117	27.68

TABLE 6. GC-MS-SIM CALIBRATION TABLE

```
                          *** External Standard  ***

Operator: JDP                                             8 Jan 87  10:02 am
Sample Info : SYR 1
Misc Info:
Integration File Name : DATA:SYR2A02A.I
                         Sequence Index: 1     Bottle Number : 2


                              Last Update:  8 Jan 87   8:13 am
                     Reference Peak Window:     5.00 Absolute Minutes
                 Non-Reference Peak Window:     0.40 Absolute Minutes
Sample Amount: 0.000  Uncalibrated Peak RF: 0.000  Multiplier: 1.667

  Peak       Int    Ret        Signal           Compound
 Num  Type Type    Time    Description            Name         Area     Amount
  1         1 PP   5.020   Mass     85.00 amu FREON 12         12893  4011 pptv
  2         1 PP   5.654   Mass     50.00 amu METHYLCHLORI      4445  2586 pptv
  3         1 BP   6.525   Mass     85.00 amu FREON 114         7067  1215 pptv
  4         1 PB   6.650   Mass     62.00 amu VINYLCHLORID      2892  1929 pptv   +
  5         1 BP   7.818   Mass     94.00 amu METHYLBROMID      2401  1729 pptv
  6         1 BB   8.421   Mass     64.00 amu ETHYLCHLORID      2134  2769 pptv   +
  7         1 BV   9.940   Mass    101.00 amu FREON 11         25069  6460 pptv
  8         1 BP  10.869   Mass     61.00 amu VINDENECHLOR      5034  1700 pptv
  9         1 BP  11.167   Mass     49.00 amu DICHLOROMETH      4803  2348 pptv
 10         1 PP  11.225   Mass     41.00 amu ALLYLCHLORID       761  8247 pptv   +
 11         1 BP  11.578   Mass    151.00 amu 3CHL3FLUETHA      5477  1673 pptv
 12         1 BP  12.492   Mass     63.00 amu 1,1DICHLOETH      5052  1738 pptv   -
 13         1 VP  13.394   Mass     61.00 amu c-1,2DICHLET      4761  1970 pptv
 14         1 PH  13.713   Mass     83.00 amu CHLOROFORM        5327  1678 pptv
 15         1 BP  14.378   Mass     62.00 amu 1,2DICHLETHA      5009  2263 pptv
 16         1 PB  14.594   Mass     97.00 amu METHCHLOROFO      6656  2334 pptv
 17         1 VP  15.009   Mass     78.00 amu BENZENE           8352  2167 pptv
 18         1 VP  15.154   Mass    117.00 amu CARBONTETRAC      5888  1915 pptv
 19         1 BB  15.821   Mass     63.00 amu 1,2DICHLPROP      3263  1799 pptv   +
 20         1 BB  16.067   Mass    130.00 amu TRICHLETHENE      4386  2109 pptv
 21         1 PB  16.941   Mass     75.00 amu c-1,3DICHLPR      2228  987.3 pptv
 22         1 BP  17.475   Mass     75.00 amu t-1,3DICHLPR      1626  689.2 pptv
 23         1 BB  17.594   Mass     97.00 amu 1,1,2CHLETHA      2721  1772 pptv
 24         1 BV  17.844   Mass     91.00 amu TOLUENE          14417  2733 pptv
 25         1 PB  18.463   Mass    107.00 amu EDB               4070  1365 pptv   +
 26         1 PH  18.989   Mass    166.00 amu TETRACHLETHE      6874  2065 pptv
 27         1 PB  19.705   Mass    112.00 amu CHLOROBENZEN      5648  1524 pptv
 28         1 BP  20.168   Mass     91.00 amu ETHYLBENZENE     11084  1842 pptv
 29         1 PB  20.372   Mass     91.00 amu m,p-XYLENE       17989  3790 pptv
 30         1 BV  20.778   Mass    104.00 amu STYRENE           3145  1695 pptv
 31         1 BH  20.887   Mass     83.00 amu TETRACHLETHA      4531  1376 pptv
 32         1 BP  20.892   Mass     91.00 amu o-XYLENE          9798  2010 pptv
 33         1 VV  22.488   Mass    105.00 amu 4-ETHYLTOLUE      7694  1481 pptv
 34         1 VB  22.609   Mass    105.00 amu 1,3,5METHBEN      6781  1705 pptv
 35         1 BB  23.144   Mass    105.00 amu 1,2,4METHBEN      7892  2095 pptv
 36         1 BV  23.273   Mass    146.00 amu m-DICHLBENZE      3046  1119 pptv
 37         1 VV  23.279   Mass     91.00 amu BENZYLCHLORI      3880  1006 pptv
 38         1 VB  23.378   Mass    146.00 amu p-DICHLBENZE      6090  2164 pptv
 39         1 BP  23.850   Mass    146.00 amu o-DICHLBENZE      2896  1249 pptv
 40         1 BB  26.673   Mass    180.00 amu 1,2,4CHLBENZ       562  767.1 pptv
 41         1 BB  27.637   Mass    225.00 amu HEXACHLBUTAD      6309  1789 pptv
```

TABLE 7. TYPICAL RETENTION TIME (MIN) AND CALIBRATION RESPONSE FACTORS (ppbv/area count) FOR TARGETED VOCs ASSOCIATED WITH FID AND ECD ANALYTICAL SYSTEM

Peak Number[1]	Compound	Retention Time (RT), minutes	FID Response Factor (RF) (ppbv/area count)	ECD Response Factor (ppbv/area count x 10^{-5})
1	Freon 12	3.65	3.465	13.89
2	Methyl chloride	4.30	0.693	
3	Freon 114	5.13	0.578	22.32
4	Vinyl chloride	5.28	0.406	
5	Methyl bromide	6.44		26.34
6	Ethyl chloride	7.06	0.413	
7	Freon 11	8.60	6.367	1.367
8	Vinylidene chloride	9.51	0.347	
9	Dichloromethane	9.84	0.903	
10	Trichlorotrifluoroethane	10.22	0.374	3.955
11	1,1-Dichloroethane	11.10	0.359	
12	cis-1,2-Dichloroethylene	11.99	0.368	
13	Chloroform	12.30	1.059	11.14
14	1,2-Dichloroethane	12.92	0.409	
15	Methyl chloroform	13.12	0.325	3.258
16	Benzene	13.51	0.117	
17	Carbon tetrachloride	13.64	1.451	1.077
18	1,2-Dichloropropane	14.26	0.214	
19	Trichloroethylene	14.50	0.327	8.910
20	cis-1,3-Dichloropropene	15.31		
21	trans-1,3-Dichloropropene	15.83		
22	1,1,2-Trichloroethane	15.93	0.336	
23	Toluene	16.17	0.092	
24	1,2-Dibromoethane (EDB)	16.78	0.366	5.137
25	Tetrachloroethylene	17.31	0.324	1.449
26	Chlorobenzene	18.03	0.120	
27	Ethylbenzene	18.51	0.092	
28	m,p-Xylene	18.72	0.095	
29	Styrene	19.12	0.143	
30	1,1,2,2-Tetrachloroethane	19.20		9.856
31	o-Xylene	19.23		
32	4-Ethyltoluene	20.82	0.100	
33	1,3,5-Trimethylbenzene	20.94	0.109	
34	1,2,4-Trimethylbenzene	21.46	0.111	
35	m-Dichlorobenzene	21.50		
36	Benzyl chloride	21.56		
37	p-Dichlorobenzene	21.67	0.188	
38	o-Dichlorobenzene	22.12	0.188	
39	1,2,4-Trichlorobenzene	24.88	0.667	
40	Hexachlorobutadiene	25.82	0.305	1.055

---

[1] Refer to Figures 15 and 16 for peak location

TABLE 8. TYPICAL RETENTION TIME (minutes) FOR SELECTED ORGANICS USING GC-FID-ECD-PID* ANALYTICAL SYSTEM

Compound	Retention Time (minutes)		
	FID	ECD	PID
Acetylene	2.984	--	--
1,3-Butadiene	3.599	--	3.594
Vinyl chloride	3.790	--	3.781
Chloromethane	5.137	--	--
Chloroethane	5.738	--	--
Bromoethane	8.154	--	--
Methylene Chloride	9.232	--	9.218
trans-1,2-Dichloroethylene	10.077	--	10.065
1,1-Dichloroethane	11.190	--	--
Chloroprene	11.502	--	11.491
Perfluorobenzene	13.077	13.078	13.069
Bromochloromethane	13.397	13.396	13.403
Chloroform	13.768	13.767	13.771
1,1,1-Trichloroethane	14.151	14.153	14.158
Carbon Tetrachloride	14.642	14.667	14.686
Benzene/1,2-Dichloroethane	15.128	--	15.114
Perfluorotoluene	15.420	15.425	15.412
Trichloroethylene	17.022	17.024	17.014
1,2-Dichloropropene	17.491	17.805	17.522
Bromodichloromethane	18.369	--	--
trans-1,3-Dichloropropylene	19.694	19.693	19.688
Toluene	20.658	--	20.653
cis-1,3-Dichloropropylene	21.461	21.357	21.357
1,1,2-Trichloroethane	21.823	--	--
Tetrachloroethylene	22.340	22.346	22.335
Dibromochloromethane	22.955	22.959	22.952
Chlorobenzene	24.866	--	24.861
m/p-Xylene	25.763	--	25.757
Styrene/o-Xylene	27.036	--	27.030
Bromofluorobenzene	28.665	28.663	28.660
1,1,2,2-Tetrachloroethane	29.225	29.227	29.228
m-Dichlorobenzene	32.347	32.345	32.342
p-Dichlorobenzene	32.671	32.669	32.666
o-Dichlorobenzene	33.885	33.883	33.880

* Varian® 3700 GC equipped with J & W Megabore® DB 624 Capillary Column (30 m X 0.53 I.D. mm) using helium carrier gas.

TABLE 9. GC-MS-SIM CALIBRATION TABLE

```
                    Last Update: 18 Dec 86   7:54 am
            Reference Peak Window:     5.00 Absolute Minutes
        Non-Reference Peak Window:     0.40 Absolute Minutes
Sample Amount: 0.000  Uncalibrated Peak RF: 0.000  Multiplier: 1.000

Ret Time Pk#    Signal Descr      Amt pptv   Lvl  [Area]    Pk-Type  Partial Name
   5.008   1    Mass    85.00 amu  13620      1 72974             1 FREON 12
   5.690   2    Mass    50.00 amu  12720      1 36447             1 METHYLCHLORID
   6.552   3    Mass    85.00 amu  8380       1 81251             1 FREON 114
   6.709   4    Mass    62.00 amu  8050       1 20118             1 VINYLCHLORIDE
   7.831   5    Mass    94.00 amu  12210      1 28265             1 METHYLBROMIDE
   8.431   6    Mass    64.00 amu  12574      1 16149             1 ETHYLCHLORIDE
   9.970   7    Mass   101.00 amu  12380      1 80088             1 FREON 11
  10.927   8    Mass    61.00 amu  7890       1 38954             1 VINDENECHLORI
  11.209   9    Mass    49.00 amu  12760      1 43507             1 DICHLOROMETHA
  11.331  10    Mass    41.00 amu  12650      1 1945              1 ALLYLCHLORIDE
  11.595  11    Mass   151.00 amu  7420       1 40530             1 3CHL3FLUETHAN
  12.502  12    Mass    63.00 amu  12710      1 61595             1 1,1DICHLOETHA
  13.403  13    Mass    61.00 amu  12630      1 50900             1 c-1,2DICHLETH
  13.747  14    Mass    83.00 amu  7670       1 40585             1 CHLOROFORM
  14.387  15    Mass    62.00 amu  9040       1 33356             1 1,2DICHLETHAN
  14.623  16    Mass    97.00 amu  8100       1 38503             1 METHCHLOROFOR
  15.038  17    Mass    78.00 amu  10760      1 69119             1 BENZENE
  15.183  18    Mass   117.00 amu  8340       1 42737             1 CARBONTETRACH
  15.829  19    Mass    63.00 amu  12780      1 38875             1 1,2DICHLPROPA
  16.096  20    Mass   130.00 amu  8750       1 30331             1 TRICHLETHENE
  16.956  21    Mass    75.00 amu  4540       1 17078             1 c-1,3DICHLPRO
  17.492  22    Mass    75.00 amu  3380       1 13294             1 t-1,3DICHLPRO
  17.610  23    Mass    97.00 amu  12690      1 32480             1 1,1,2CHLETHAN
  17.862  24    Mass    91.00 amu  10010      1 88036             1 TOLUENE
  18.485  25    Mass   107.00 amu  6710       1 33350             1 EDB
  19.012  26    Mass   166.00 amu  7830       1 43454             1 TETRACHLETHEN
  19.729  27    Mass   112.00 amu  7160       1 44224             1 CHLOROBENZENE
  20.195  28    Mass    91.00 amu  12740      1 127767            1 ETHYLBENZENE
  20.407  29    Mass    91.00 amu  25400      1 200973            1 m,p-XYLENE
  20.806  30    Mass   104.00 amu  12390      1 38332             1 STYRENE
  20.916  31    Mass    83.00 amu  11690      1 64162             1 TETRACHLETHAN
  20.921  32    Mass    91.00 amu  11085      1 90096             1 o-XYLENE
  22.528  33    Mass   105.00 amu  12560      1 108747            1 4-ETHYLTOLUEN
  22.648  34    Mass   105.00 amu  12620      1 83666             1 1,3,5METHBENZ
  23.179  35    Mass   105.00 amu  12710      1 79833             1 1,2,4METHBENZ
  23.307  36    Mass   146.00 amu  12650      1 57409             1 m-DICHLBENZEN
  23.317  37    Mass    91.00 amu  7900       1 50774             1 BENZYLCHLORID
  23.413  38    Mass   146.00 amu  12390      1 58127             1 p-DICHLBENZEN
  23.885  39    Mass   146.00 amu  13510      1 52233             1 o-DICHLBENZEN
  26.714  40    Mass   180.00 amu  15520      1 18967             1 1,2,4CHLBENZE
  27.680  41    Mass   225.00 amu  7470       1 43920             1 HEXACHLBUTADI
```

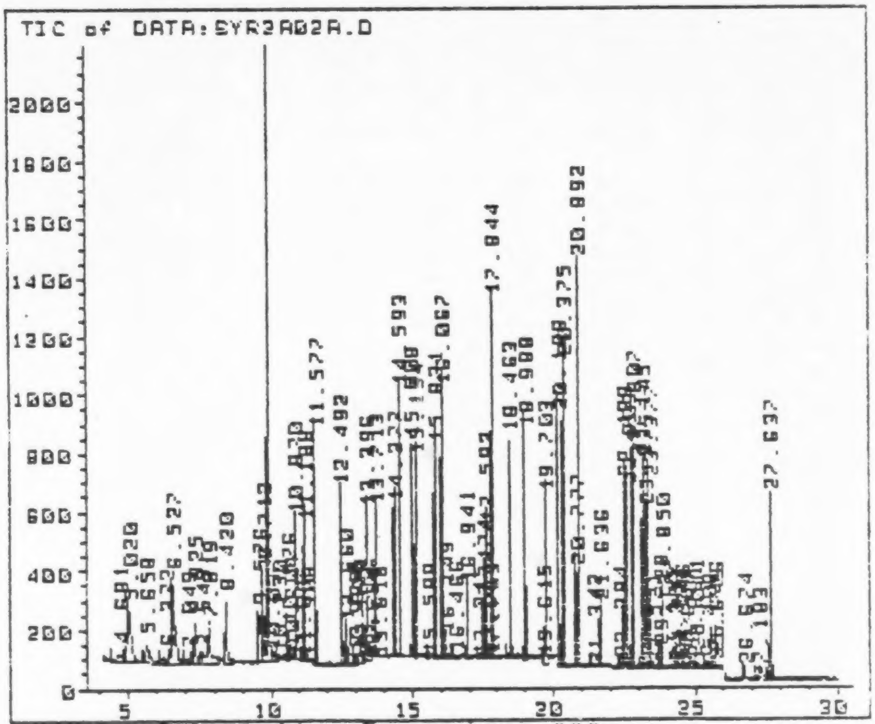
TABLE 10. EXAMPLE OF HARD-COPY OF GC-MS-SIM ANALYSIS

```
Data file: DATA:SYR2A02A.D
File type: GC / MS DATA FILE

Name Info: SYR 1
Misc Info:
Operator : JDF

Date      :  8 Jan 87  10:02 am
Instrment: MS_5970
Inlet     : GC

Sequence index :     1
Als bottle num :     2
Replicate num  :     1
```



```
*** Integration Parameters ***

FALSE : Shoulder Detection Enabled
0.020 : Expected Peak Width (Min)
   11 : Initial Peak Detection Threshold

4.000  THRESHOLD       5.000
4.000  PEAK_WIDTH       0.200
9.800  PEAK_WIDTH       0.060
```

TABLE 10. EXAMPLE OF HARD-COPY OF GC-MS-SIM ANALYSIS (cont.)

```
                                                                    8 Jan 87   10:02 am
Operator: JDF
Sample Info : SYR 1
Misc Info:
Integration File Name : DATA:SYR2A02A.I
                         Sequence Index: 1      Bottle Number : 2


                          Last Update:  8 Jan 87    8:13 am
                   Reference Peak Window:     5.00 Absolute Minutes
               Non-Reference Peak Window:     0.40 Absolute Minutes
 Sample Amount: 0.000  Uncalibrated Peak RF: 0.000  Multiplier: 1.667

   Peak        Int    Ret        Signal              Compound
  Num   Type  Type    Time     Description             Name          Area     Amount
   1          1 PP    5.020    Mass     85.00 amu FREON 12           12893    4011 pptv
   2          1 PP    5.654    Mass     50.00 amu METHYLCHLORI        4445    2586 pptv
   3          1 BP    6.525    Mass     85.00 amu FREON 114           7067    1215 pptv
   4          1 PB    6.650    Mass     62.00 amu VINYLCHLORID        2892    1929 pptv   *
   5          1 BP    7.818    Mass     94.00 amu METHYLBROMID        2401    1729 pptv
   6          1 BB    8.421    Mass     64.00 amu ETHYLCHLORID        2134    2769 pptv   *
   7          1 BV    9.940    Mass    101.00 amu FREON 11           25069    6460 pptv
   8          1 BP   10.869    Mass     61.00 amu VINDENECHLOR        5034    1700 pptv
   9          1 BP   11.187    Mass     49.00 amu DICHLOROMETH        4803    2348 pptv
  10          1 PP   11.225    Mass     41.00 amu ALLYLCHLORID         761    8247 pptv   *
  11          1 BP   11.578    Mass    151.00 amu 3CHL3FLUETHA        5477    1672 pptv
  12          1 BP   12.492    Mass     63.00 amu 1,1DICHLOETH        5052    1738 pptv   -
  13          1 VP   13.394    Mass     61.00 amu c-1,2DICHLET        4761    1970 pptv
  14          1 PH   13.713    Mass     83.00 amu CHLOROFORM          5327    1678 pptv
  15          1 BP   14.378    Mass     62.00 amu 1,2DICHLETHA        5009    2263 pptv
  16          1 PB   14.594    Mass     97.00 amu METHCHLOROFO        6656    2334 pptv
  17          1 VP   15.009    Mass     78.00 amu BENZENE             8352    2167 pptv
  18          1 VP   15.154    Mass    117.00 amu CARBONTETRAC        5888    1915 pptv
  19          1 BB   15.821    Mass     63.00 amu 1,2DICHLPROP        3263    1799 pptv   *
  20          1 BB   16.067    Mass    130.00 amu TRICHLETHENE        4386    2109 pptv
  21          1 PB   16.941    Mass     75.00 amu c-1,3DICHLPR        2228    987.3 pptv
  22          1 BP   17.475    Mass     75.00 amu t-1,3DICHLPR        1626    689.2 pptv
  23          1 BB   17.594    Mass     97.00 amu 1,1,2CHLETHA        2721    1772 pptv
  24          1 BV   17.844    Mass     91.00 amu TOLUENE            14417    2733 pptv
  25          1 PB   18.463    Mass    107.00 amu EDB                 4070    1365 pptv   *
  26          1 PH   18.989    Mass    166.00 amu TETRACHLETHE        6874    2065 pptv
  27          1 PB   19.705    Mass    112.00 amu CHLOROBENZEN        5648    1524 pptv
  28          1 BP   20.168    Mass     91.00 amu ETHYLBENZENE       11084    1842 pptv
  29          1 PB   20.372    Mass     91.00 amu m,p-XYLENE         17989    3790 pptv
  30          1 BV   20.778    Mass    104.00 amu STYRENE             3145    1695 pptv
  31          1 BH   20.887    Mass     83.00 amu TETRACHLETHA        4531    1376 pptv
  32          1 BP   20.892    Mass     91.00 amu o-XYLENE            9798    2010 pptv
  33          1 VV   22.488    Mass    105.00 amu 4-ETHYLTOLUE        7694    1481 pptv
  34          1 VB   22.609    Mass    105.00 amu 1,3,5METHBEN        6781    1705 pptv
  35          1 BB   23.144    Mass    105.00 amu 1,2,4METHBEN        7892    2095 pptv
  36          1 BV   23.273    Mass    146.00 amu m-DICHLBENZE        3046    1119 pptv
  37          1 VV   23.279    Mass     91.00 amu BENZYLCHLORI        3880    1006 pptv
  38          1 VB   23.378    Mass    146.00 amu p-DICHLBENZE        6090    2164 pptv
  39          1 BP   23.850    Mass    146.00 amu o-DICHLBENZE        2896    1249 pptv
  40          1 BB   26.673    Mass    180.00 amu 1,2,4CHLBENZ         562    767.1 pptv
  41          1 BB   27.637    Mass    225.00 amu HEXACHLBUTAD        6309    1789 pptv
```

Reproduced from best available copy.

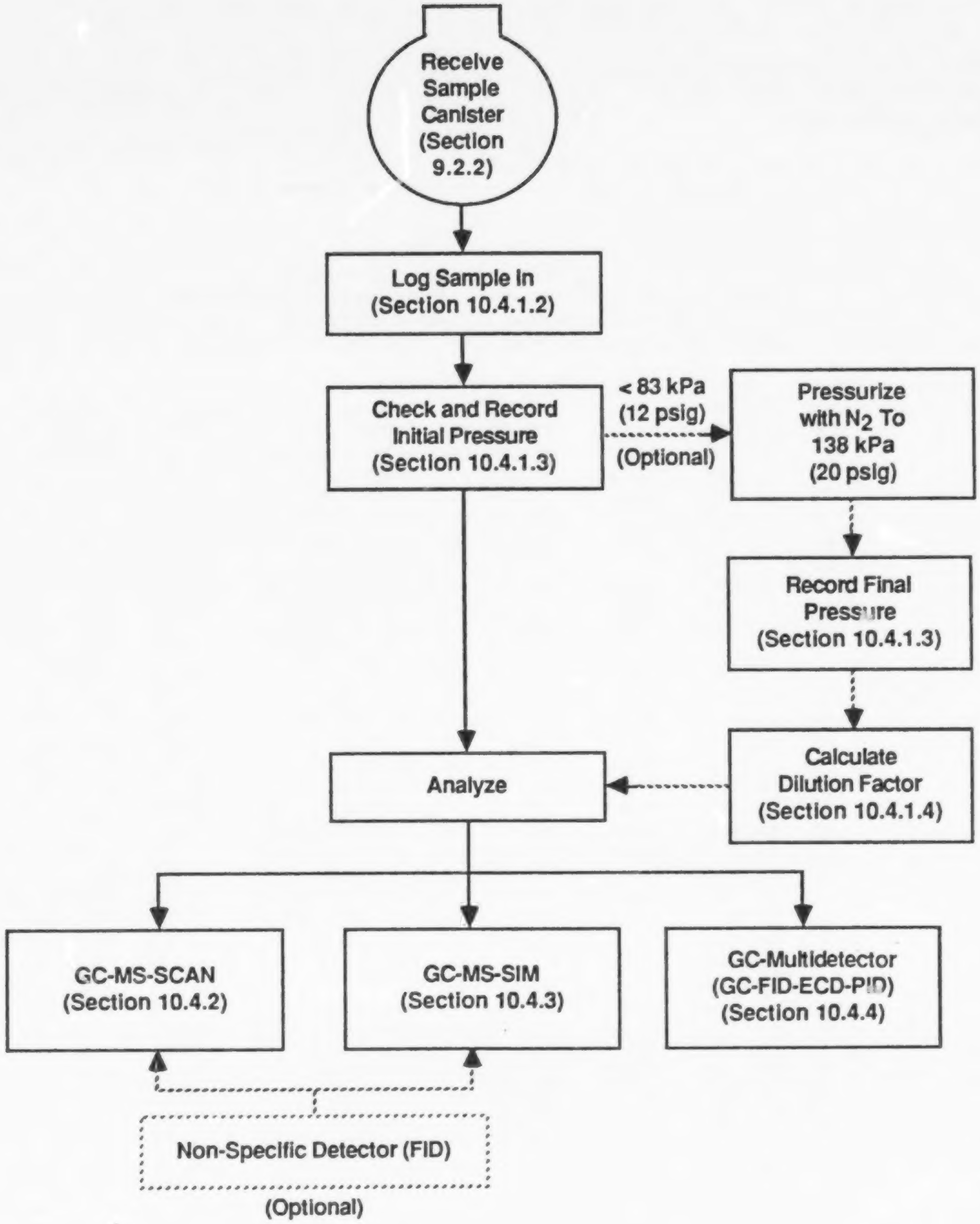

Receive Sample Canister (Section 9.2.2)
Log Sample In (Section 10.4.1.2)
Check and Record Initial Pressure (Section 10.4.1.3)
< 83 kPa (12 psig)
(Optional)
Pressurize with N_2 To 138 kPa (20 psig)
Record Final Pressure (Section 10.4.1.3)
Calculate Dilution Factor (Section 10.4.1.4)
Analyze
GC-MS-SCAN (Section 10.4.2)
GC-MS-SIM (Section 10.4.3)
GC-Multidetector (GC-FID-ECD-PID) (Section 10.4.4)
Non-Specific Detector (FID)
(Optional)

FIGURE 1. ANALYTICAL SYSTEMS AVAILABLE FOR CANISTER VOC IDENTIFICATION AND QUANTITATION

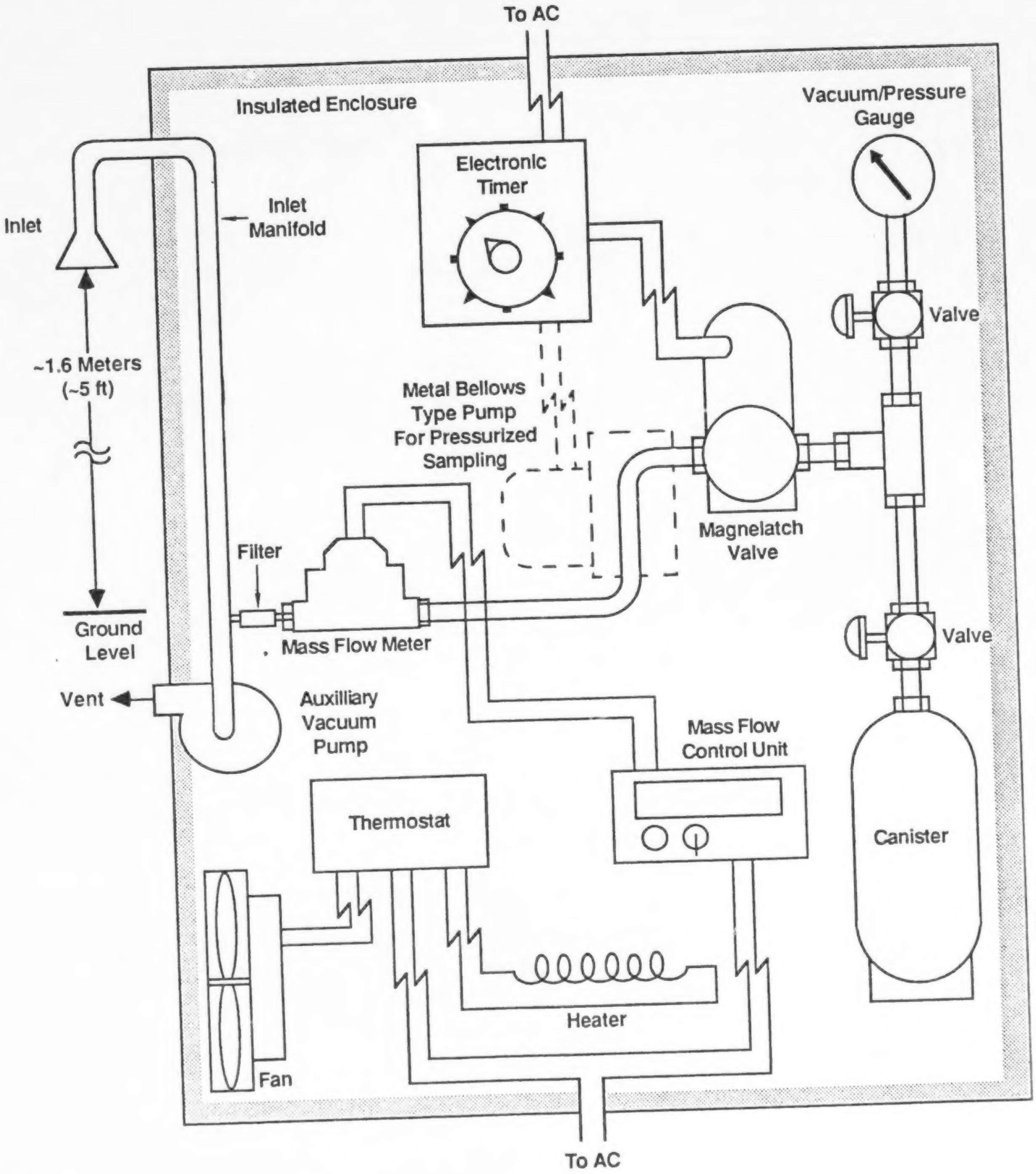

To AC
Insulated Enclosure
Vacuum/Pressure Gauge
Electronic Timer
Inlet
Inlet Manifold
Valve
~1.6 Meters (~5 ft)
Metal Bellows Type Pump For Pressurized Sampling
Magnelatch Valve
Filter
Ground Level
Mass Flow Meter
Valve
Vent
Auxilliary Vacuum Pump
Mass Flow Control Unit
Thermostat
Canister
Heater
Fan
To AC

FIGURE 2. SAMPLER CONFIGURATION FOR SUBATMOSPHERIC PRESSURE OR PRESSURIZED CANISTER SAMPLING

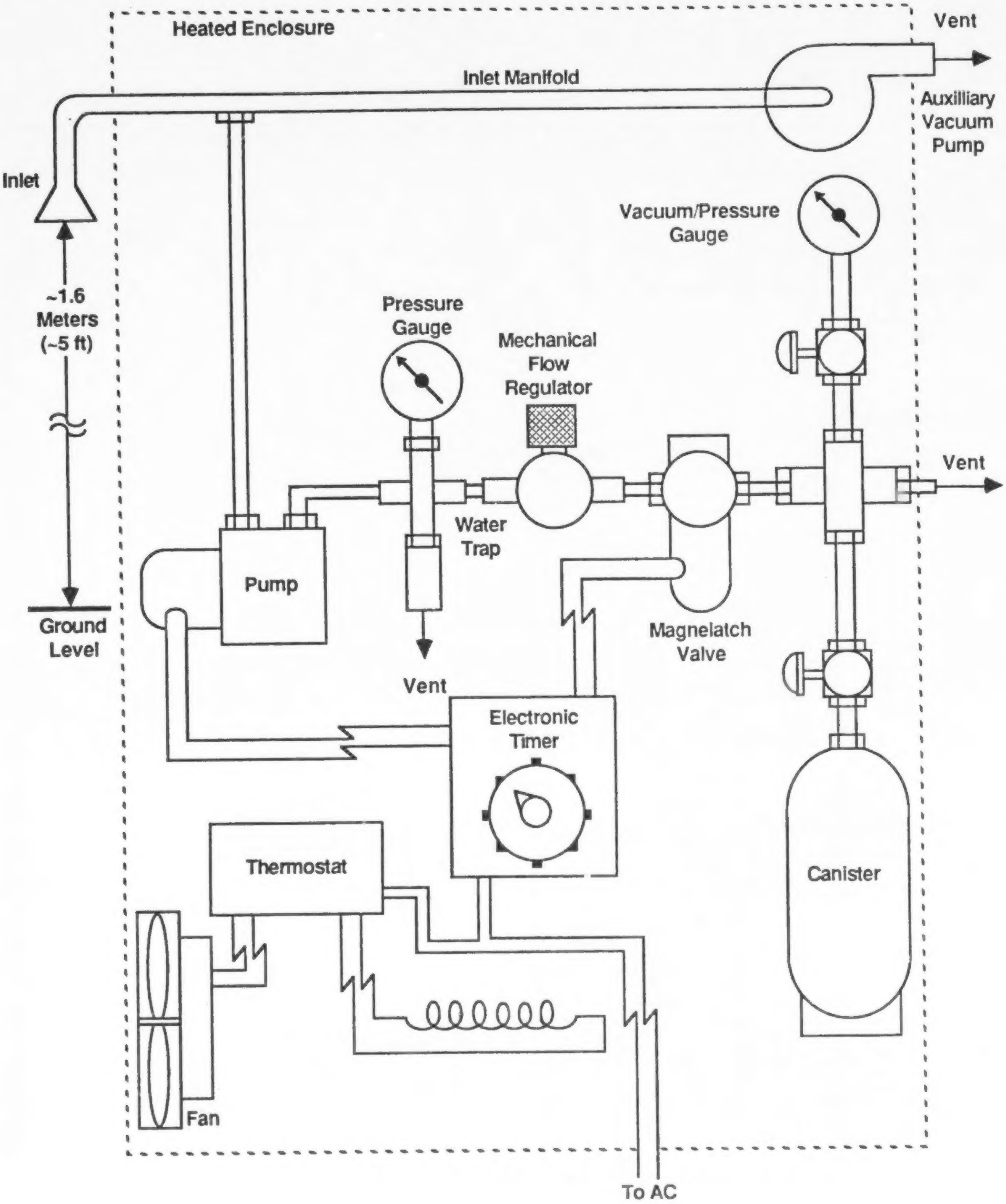

Heated Enclosure
Vent
Inlet Manifold
Auxilliary
Vacuum
Pump
Inlet
Vacuum/Pressure
Gauge
~1.6
Meters
(~5 ft)
Pressure
Gauge
Mechanical
Flow
Regulator
Vent
Water
Trap
Pump
Ground
Level
Magnelatch
Valve
Vent
Electronic
Timer
Thermostat
Canister
Fan
To AC

FIGURE 3. ALTERNATIVE SAMPLER CONFIGURATION FOR PRESSURIZED CANISTER SAMPLING

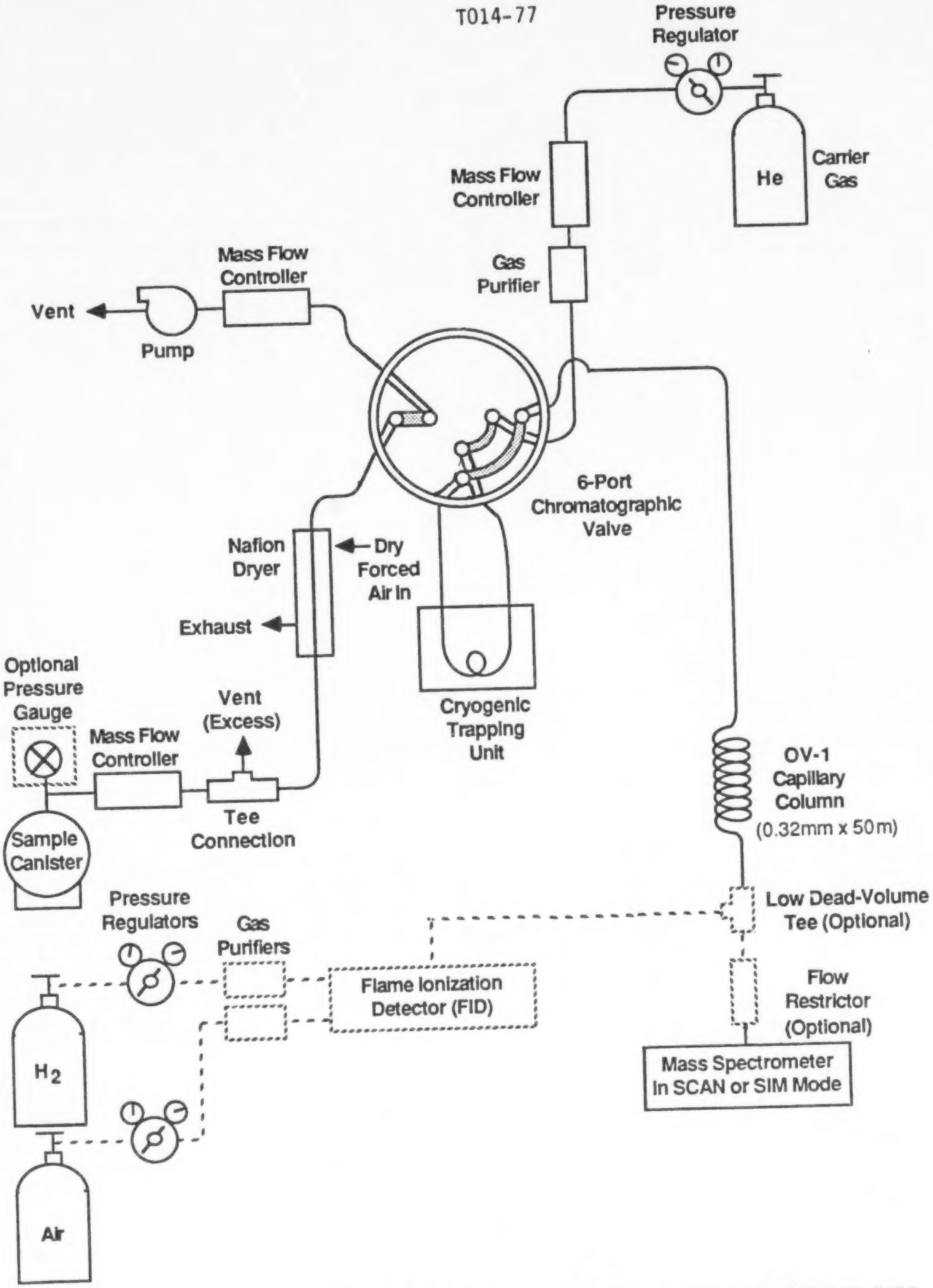

Pressure Regulator
He
Carrier Gas
Mass Flow Controller
Gas Purifier
Mass Flow Controller
Vent
Pump
6-Port Chromatographic Valve
Nafion Dryer
Dry Forced Air In
Exhaust
Cryogenic Trapping Unit
Optional Pressure Gauge
Mass Flow Controller
Vent (Excess)
Tee Connection
Sample Canister
OV-1 Capillary Column (0.32mm x 50m)
Low Dead-Volume Tee (Optional)
Pressure Regulators
Gas Purifiers
Flame Ionization Detector (FID)
Flow Restrictor (Optional)
Mass Spectrometer In SCAN or SIM Mode
H2
Air

FIGURE 4. CANISTER ANALYSIS UTILIZING GC-MS-SCAN-SIM ANALYTICAL SYSTEM WITH OPTIONAL FLAME IONIZATION DETECTOR WITH THE 6-PORT CHROMATOGRAPHIC VALVE IN THE SAMPLE DESORPTION MODE

T014-78

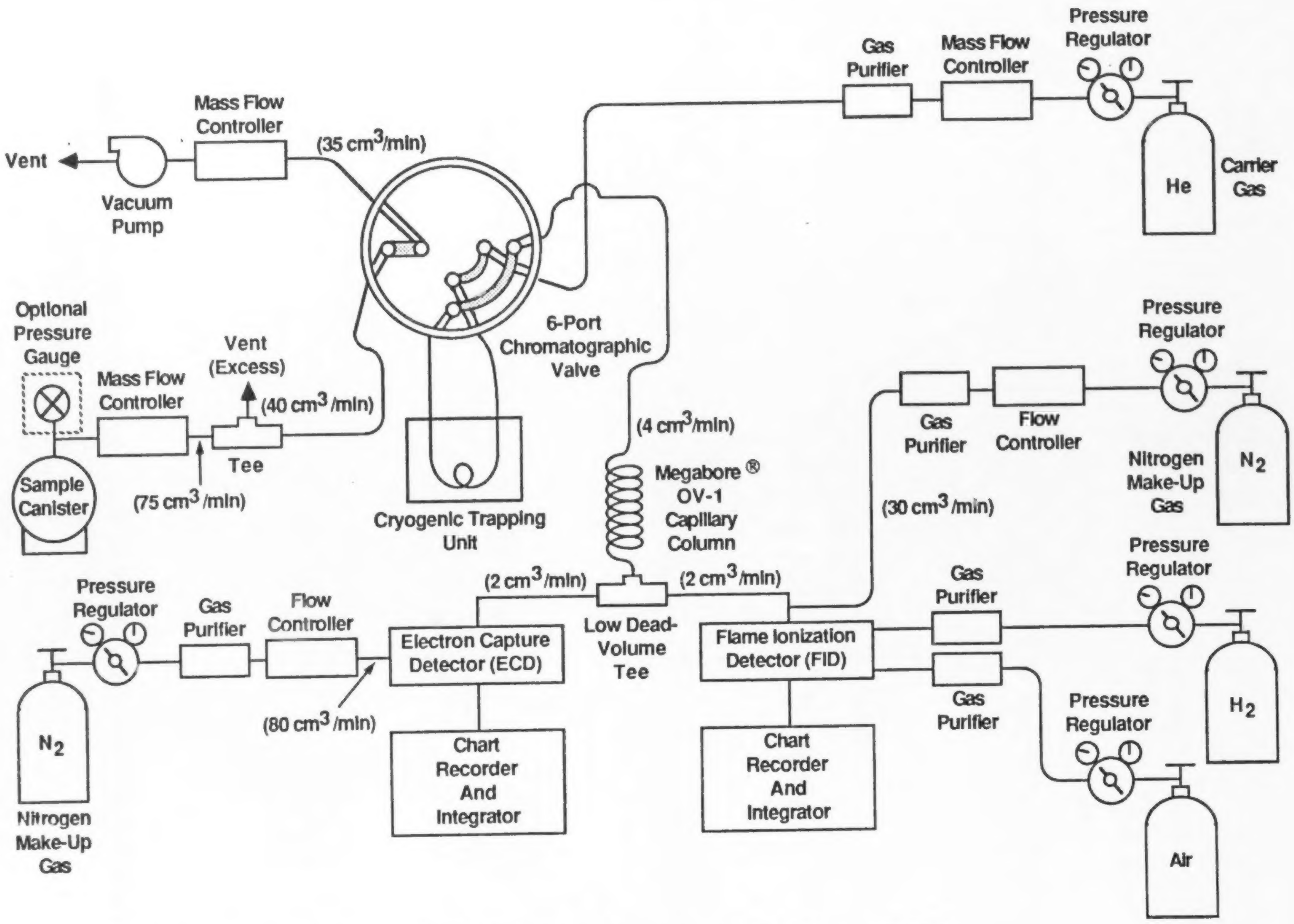

Gas Purifier
Mass Flow Controller
Pressure Regulator
He
Carrier Gas
Mass Flow Controller
(35 cm³/min)
Vent
Vacuum Pump
Optional Pressure Gauge
Mass Flow Controller
Vent (Excess)
(40 cm³/min)
Tee
Sample Canister
(75 cm³/min)
6-Port Chromatographic Valve
Cryogenic Trapping Unit
(4 cm³/min)
Megabore ® OV-1 Capillary Column
Pressure Regulator
Gas Purifier
Flow Controller
Nitrogen Make-Up Gas
N2
(30 cm³/min)
Pressure Regulator
Gas Purifier
(2 cm³/min)
(2 cm³/min)
Low Dead-Volume Tee
Pressure Regulator
Gas Purifier
Flow Controller
Electron Capture Detector (ECD)
Flame Ionization Detector (FID)
H2
N2
(80 cm³/min)
Gas Purifier
Pressure Regulator
Chart Recorder And Integrator
Chart Recorder And Integrator
Nitrogen Make-Up Gas
Air

FIGURE 5. GC-FID-ECD ANALYTICAL SYSTEM WITH THE 6-PORT CHROMATOGRAPHIC VALVE IN THE SAMPLE DESORPTION MODE

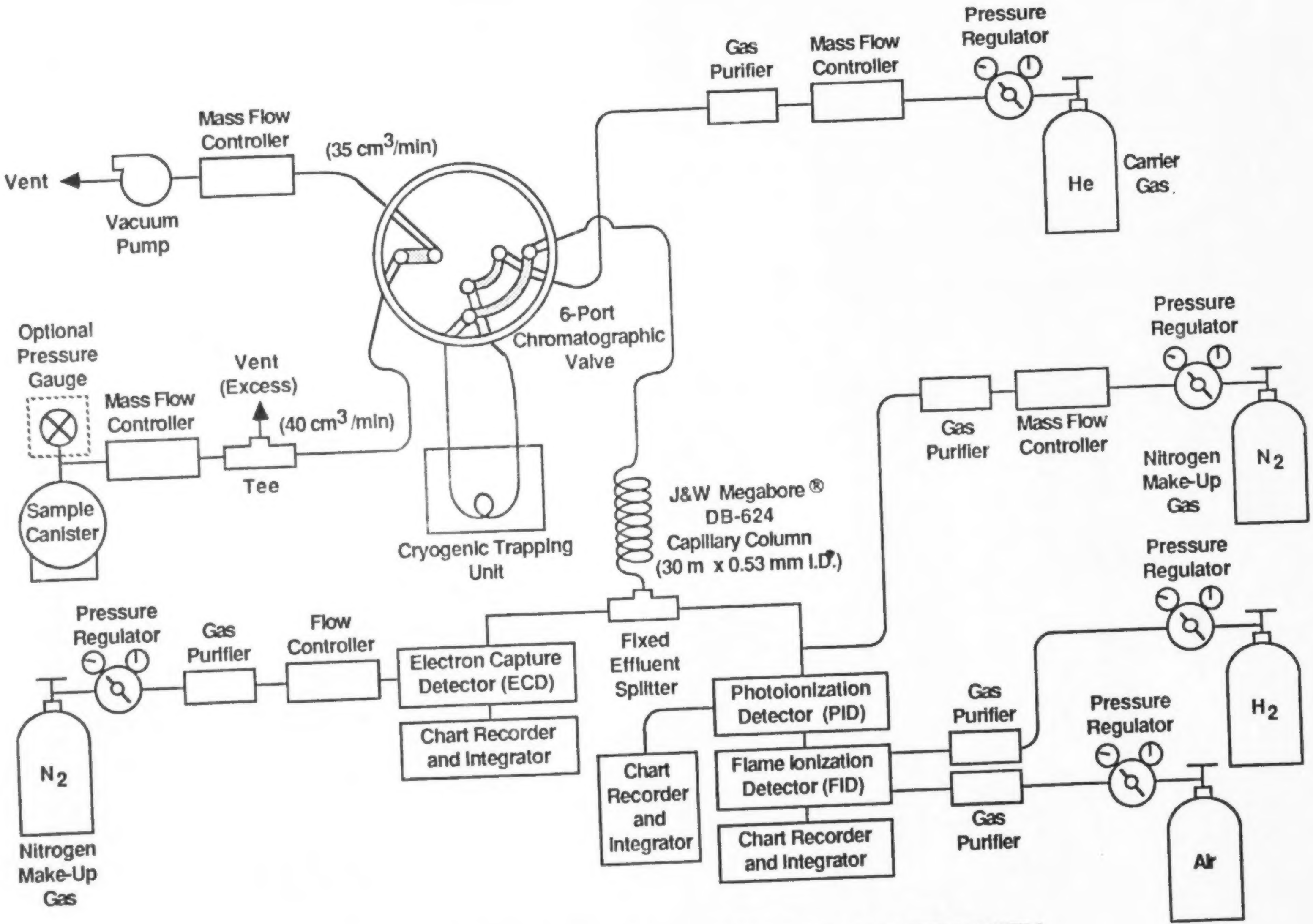

Vent
Vacuum Pump
Mass Flow Controller
(35 cm3/min)
Gas Purifier
Mass Flow Controller
Pressure Regulator
He
Carrier Gas.
Optional Pressure Gauge
Mass Flow Controller
Vent (Excess)
(40 cm3 /min)
Tee
Sample Canister
6-Port Chromatographic Valve
Cryogenic Trapping Unit
J&W Megabore ®
DB-624
Capillary Column
(30 m x 0.53 mm I.D.)
Gas Purifier
Mass Flow Controller
Pressure Regulator
Nitrogen Make-Up Gas
N2
Pressure Regulator
Gas Purifier
Flow Controller
Electron Capture Detector (ECD)
Chart Recorder and Integrator
Fixed Effluent Splitter
Photoionization Detector (PID)
Chart Recorder and Integrator
Flame Ionization Detector (FID)
Chart Recorder and Integrator
Gas Purifier
Gas Purifier
Pressure Regulator
H2
Pressure Regulator
Air
N2
Nitrogen Make-Up Gas

FIGURE 6. SYSTEM CONFIGURATION ASSOCIATED WITH THE GC-FID-ECD-PID ANALYTICAL SYSTEM WITH THE 6-PORT CHROMATOGRAPHIC VALVE IN THE SAMPLE DESORPTION MODE

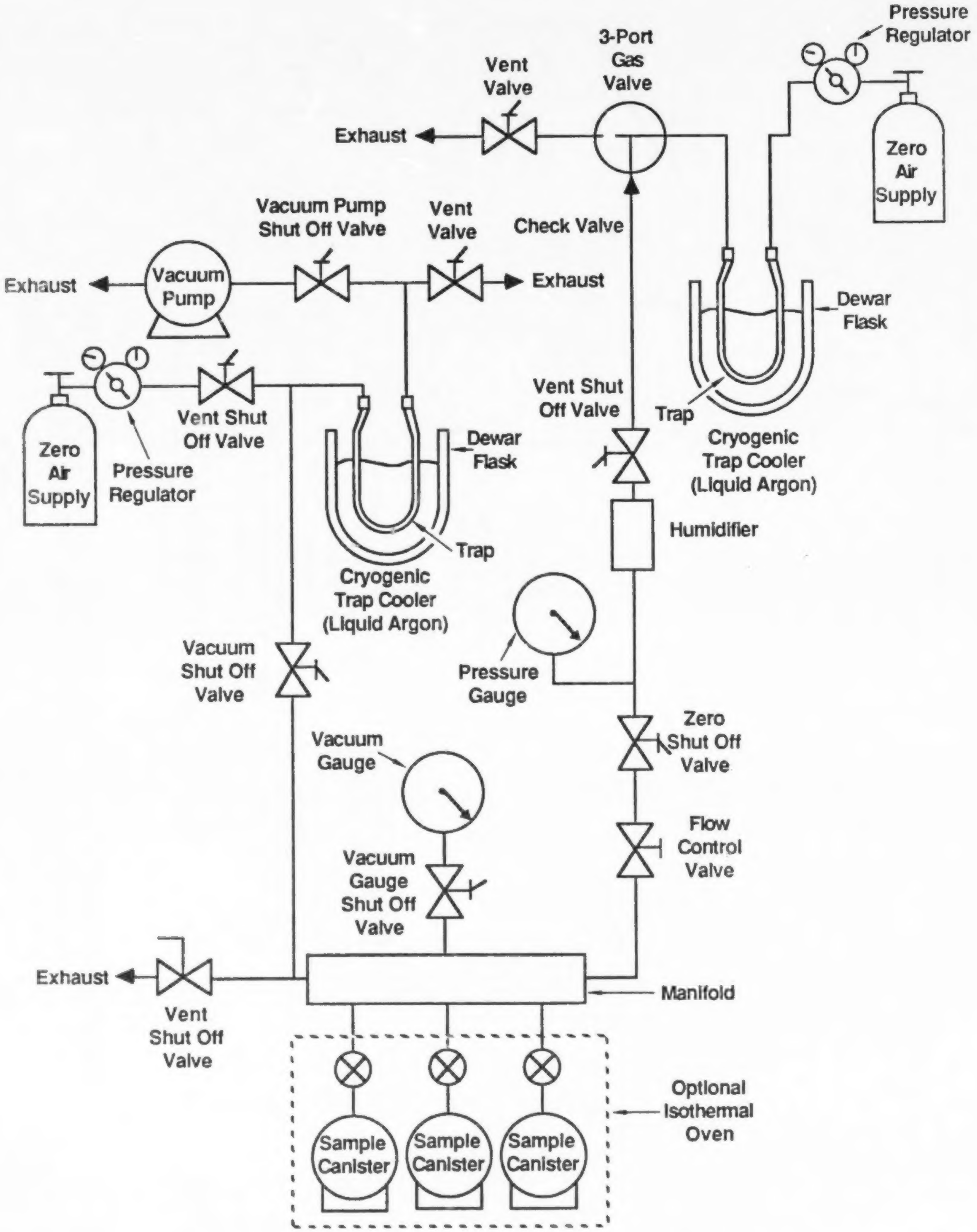

Pressure Regulator
3-Port Gas Valve
Vent Valve
Exhaust
Zero Air Supply
Vacuum Pump Shut Off Valve
Vent Valve
Check Valve
Exhaust
Vacuum Pump
Exhaust
Dewar Flask
Vent Shut Off Valve
Trap
Vent Shut Off Valve
Dewar Flask
Cryogenic Trap Cooler (Liquid Argon)
Zero Air Supply
Pressure Regulator
Humidifier
Trap
Cryogenic Trap Cooler (Liquid Argon)
Vacuum Shut Off Valve
Pressure Gauge
Zero Shut Off Valve
Vacuum Gauge
Flow Control Valve
Vacuum Gauge Shut Off Valve
Exhaust
Manifold
Vent Shut Off Valve
Optional Isothermal Oven
Sample Canister
Sample Canister
Sample Canister

FIGURE 7. CANISTER CLEANING SYSTEM

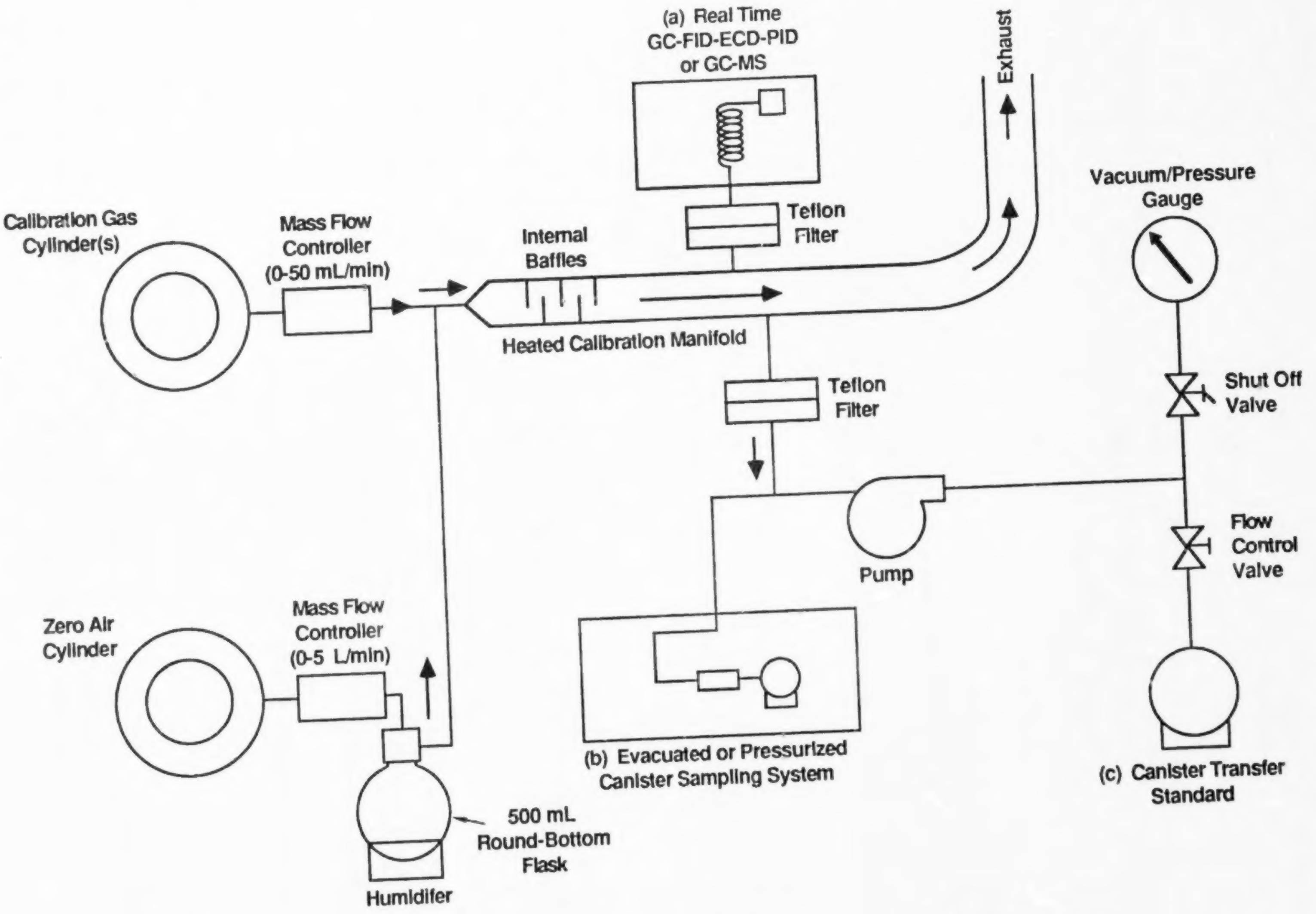
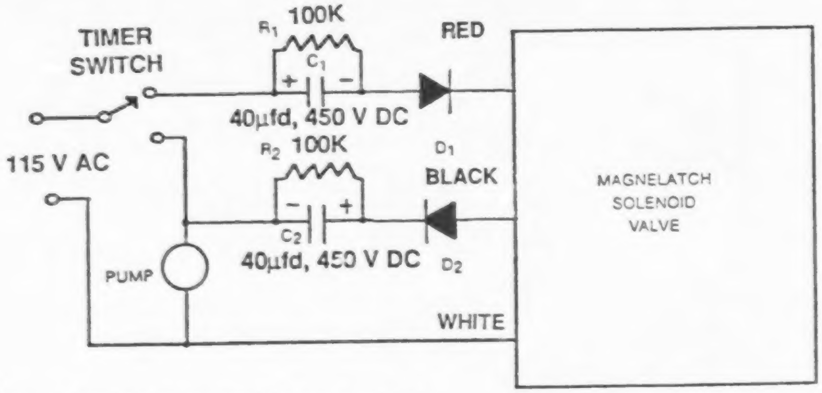

(a) Real Time
GC-FID-ECD-PID
or GC-MS
Exhaust
Calibration Gas
Cylinder(s)
Mass Flow
Controller
(0-50 mL/min)
Internal
Baffles
Teflon
Filter
Vacuum/Pressure
Gauge
Heated Calibration Manifold
Teflon
Filter
Shut Off
Valve
Pump
Flow
Control
Valve
Zero Air
Cylinder
Mass Flow
Controller
(0-5 L/min)
(b) Evacuated or Pressurized
Canister Sampling System
(c) Canister Transfer
Standard
500 mL
Round-Bottom
Flask
Humidifer

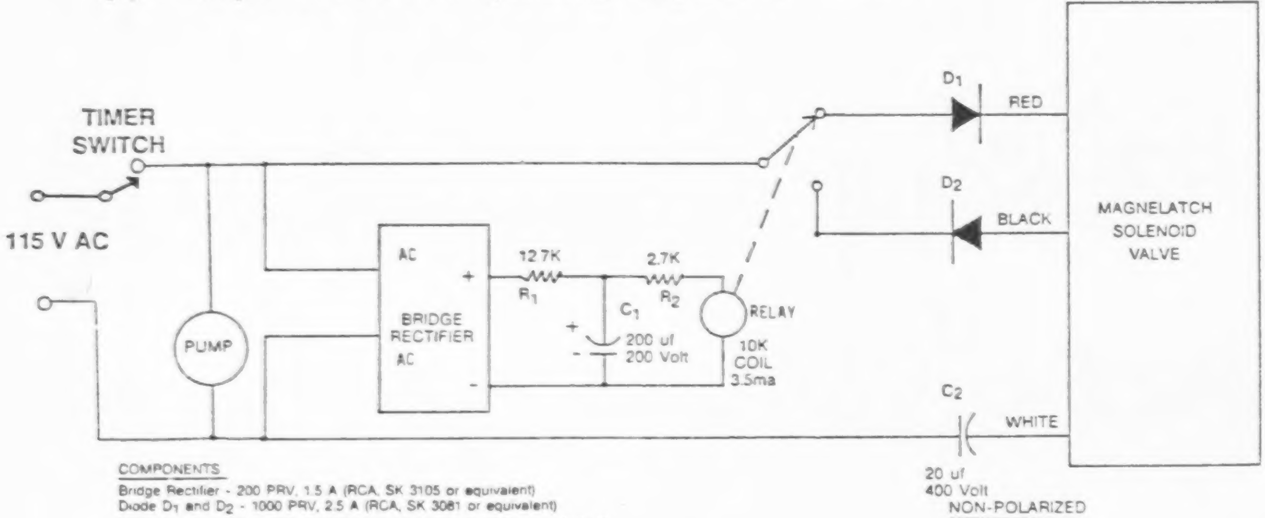
FIGURE 8. SCHEMATIC OF CALIBRATION SYSTEM AND MANIFOLD FOR (a) ANALYTICAL SYSTEM CALIBRATION, (b) TESTING CANISTER SAMPLING SYSTEM AND (c) PREPARING CANISTER TRANSFER STANDARDS.


TIMER
SWITCH
115 V AC
R1 100K
C1
+
−
40µfd, 450 V DC
R2 100K
−
+
C2
40µfd, 450 V DC
RED
D1
BLACK
D2
WHITE
PUMP
MAGNELATCH
SOLENOID
VALVE

COMPONENTS

Capacitor C_1 and C_2 - 40 uf, 450 VDC (Sprague Atom® TVA 1712 or equivalent)
Resister R_1 and R_2 - 0.5 watt, 5% tolerance
Diode D_1 and D_2 - 1000 PRV, 2.5 A (RCA, SK 3081 or equivalent)

(a). Simple Circuit For Operating Magnelatch Valve


TIMER
SWITCH
115 V AC
PUMP
AC
+
BRIDGE
RECTIFIER
AC
−
12.7K
R1
2.7K
R2
C1
+
−
200 uf
200 Volt
RELAY
10K
COIL
3.5ma
D1
RED
D2
BLACK
C2
WHITE
20 uf
400 Volt
NON-POLARIZED
MAGNELATCH
SOLENOID
VALVE

COMPONENTS

Bridge Rectifier - 200 PRV, 1.5 A (RCA, SK 3105 or equivalent)
Diode D_1 and D_2 - 1000 PRV, 2.5 A (RCA, SK 3081 or equivalent)
Capacitor C_1 - 200 uf, 250 VDC (Sprague Atom® TVA 1528 or equivalent)
Capacitor C_2 - 20 uf, 400 VDC Non-Polarized (Sprague Atom® TVAN 1652 or equivalent)
Relay - 10,000 ohm coil, 3.5 ma (AMF Potter and Brumfield, KCP 5, or equivalent)
Resister R_1 and R_2 - 0.5 watt, 5% tolerance

(b). Improved Circuit Designed To Handle Power Interruptions

FIGURE 9. ELECTRICAL PULSE CIRCUITS FOR DRIVING SKINNER MAGNELATCH SOLENOID VALVE WITH A MECHANICAL TIMER

CANISTER SAMPLING FIELD DATA SHEET

A. GENERAL INFORMATION

SITE LOCATION:

SITE ADDRESS:

SAMPLING DATE:

SHIPPING DATE:

CANISTER SERIAL NO.:

SAMPLER ID:

OPERATOR:

CANISTER LEAK CHECK DATE:

B. SAMPLING INFORMATION

TEMPERATURE

	INTERIOR	AMBIENT	MAXIMUM	MINIMUM
START			☒	☒
STOP				

PRESSURE

CANISTER PRESSURE	
☒	

SAMPLING TIMES

	LOCAL TIME	ELAPSED TIME METER READING
START		
STOP		

FLOW RATES

MANIFOLD FLOW RATE	CANISTER FLOW RATE	FLOW CONTROLLER READOUT

SAMPLING SYSTEM CERTIFICATION DATE:

QUARTERLY RECERTIFICATION DATE:

C. LABORATORY INFORMATION

DATE RECEIVED:

RECEIVED BY:

INITIAL PRESSURE:

FINAL PRESSURE:

DILUTION FACTOR:

ANALYSIS

- GC-FID-ECD DATE:
- GC-MSD-SCAN DATE:
- GC-MSD-SIM DATE:

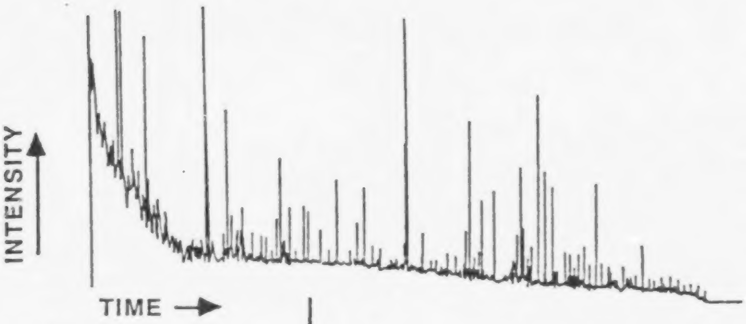
RESULTS*:

- GC-FID-ECD:
- GC-MSD-SCAN:
- GC-MSD-SIM:

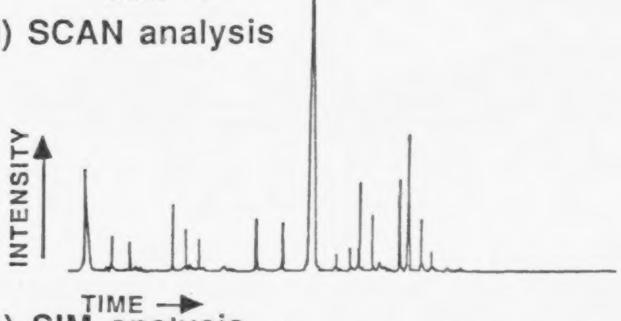
SIGNATURE/TITLE

* ATTACH DATA SHEETS

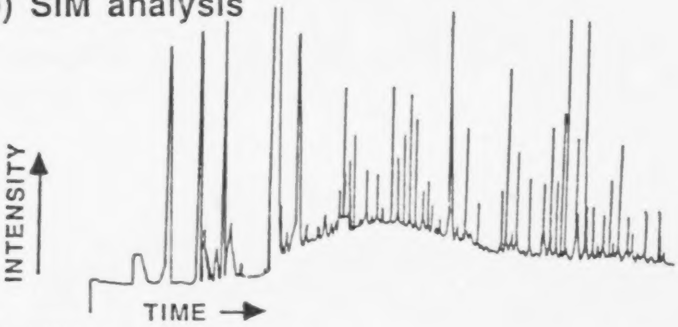
FIGURE 10. CANISTER SAMPLING FIELD DATA SHEET



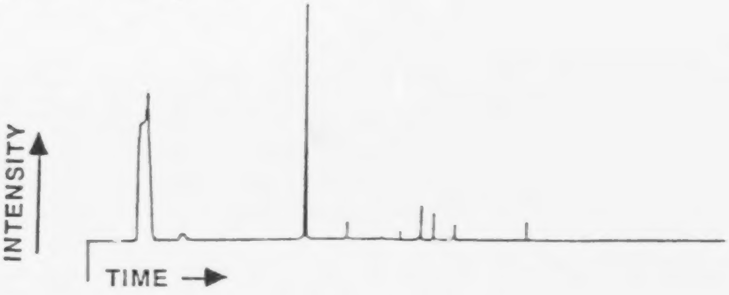
(a) SCAN analysis



(b) SIM analysis



(c) FID analysis



(d) ECD analysis

FIGURE 11. TYPICAL CHROMATOGRAMS OF A VOC SAMPLE ANALYZED BY GC-MS-SCAN-SIM MODE AND GC-MULTIDETECTOR MODE

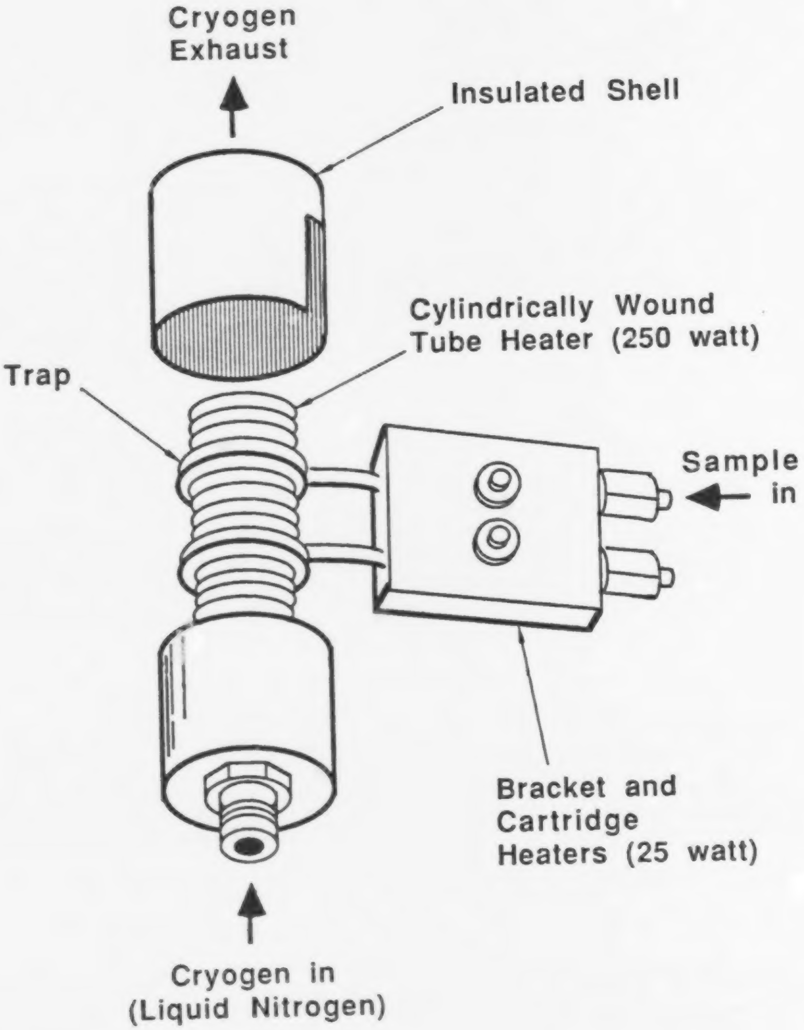

Cryogen Exhaust
Insulated Shell
Cylindrically Wound Tube Heater (250 watt)
Trap
Sample in
Bracket and Cartridge Heaters (25 watt)
Cryogen in (Liquid Nitrogen)

FIGURE 12. CRYOGENIC TRAPPING UNIT

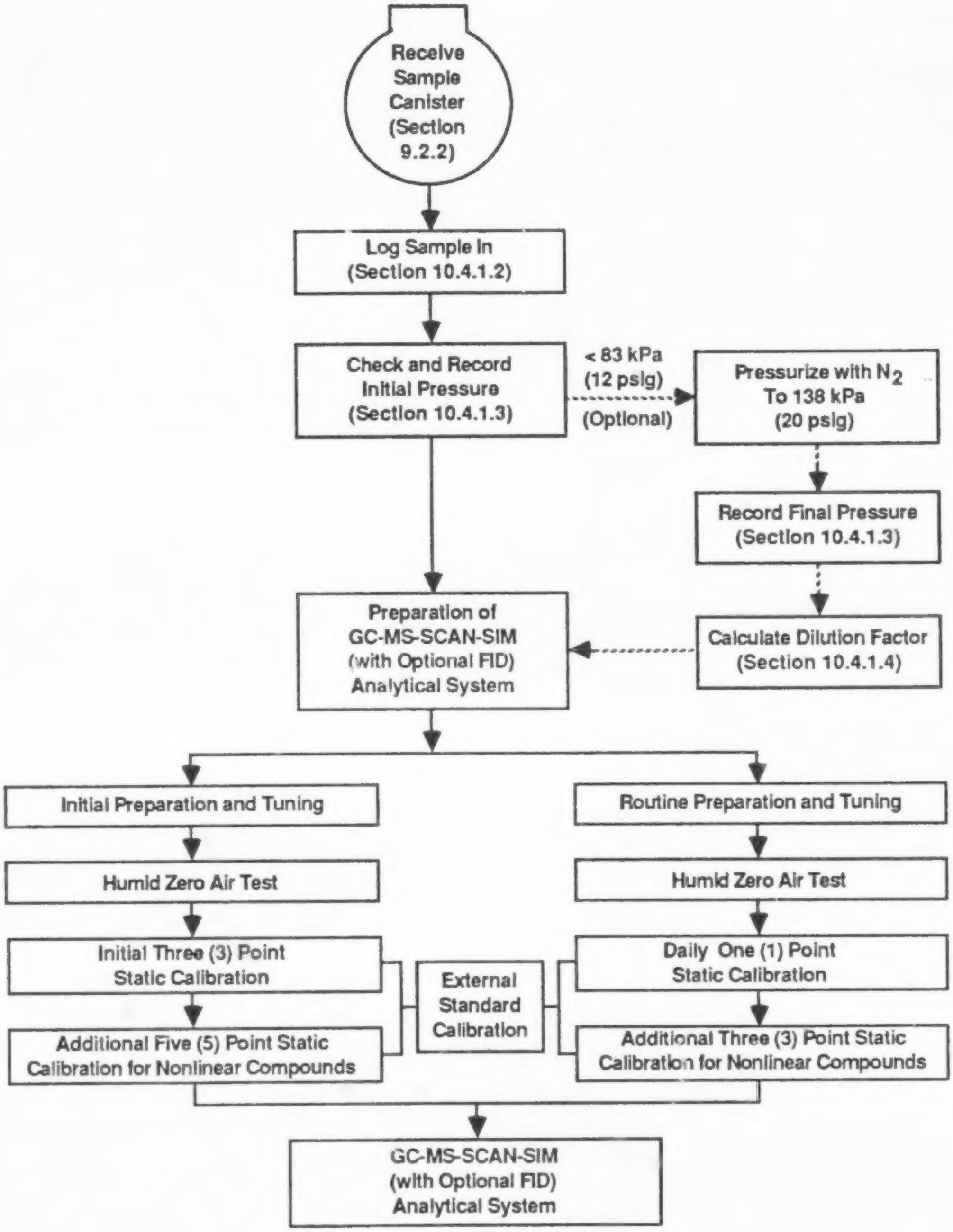

Receive Sample Canister (Section 9.2.2)
Log Sample In (Section 10.4.1.2)
Check and Record Initial Pressure (Section 10.4.1.3)
< 83 kPa (12 psig) (Optional)
Pressurize with N2 To 138 kPa (20 psig)
Record Final Pressure (Section 10.4.1.3)
Calculate Dilution Factor (Section 10.4.1.4)
Preparation of GC-MS-SCAN-SIM (with Optional FID) Analytical System
Initial Preparation and Tuning
Routine Preparation and Tuning
Humid Zero Air Test
Humid Zero Air Test
Initial Three (3) Point Static Calibration
External Standard Calibration
Daily One (1) Point Static Calibration
Additional Five (5) Point Static Calibration for Nonlinear Compounds
Additional Three (3) Point Static Calibration for Nonlinear Compounds
GC-MS-SCAN-SIM (with Optional FID) Analytical System

FIGURE 13. FLOWCHART OF GC-MS-SCAN-SIM ANALYTICAL SYSTEM PREPARATION (WITH OPTIONAL FID SYSTEM)

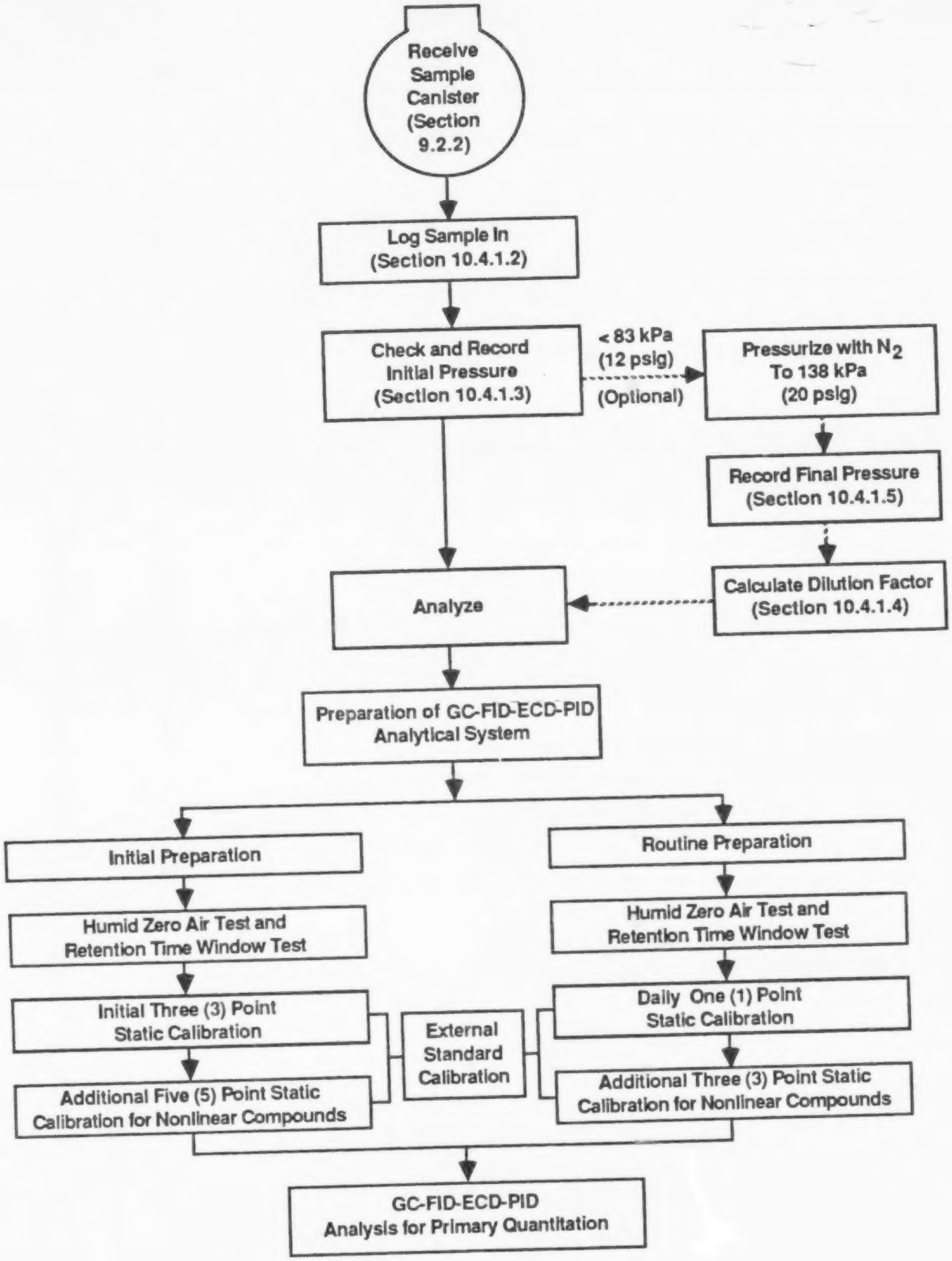
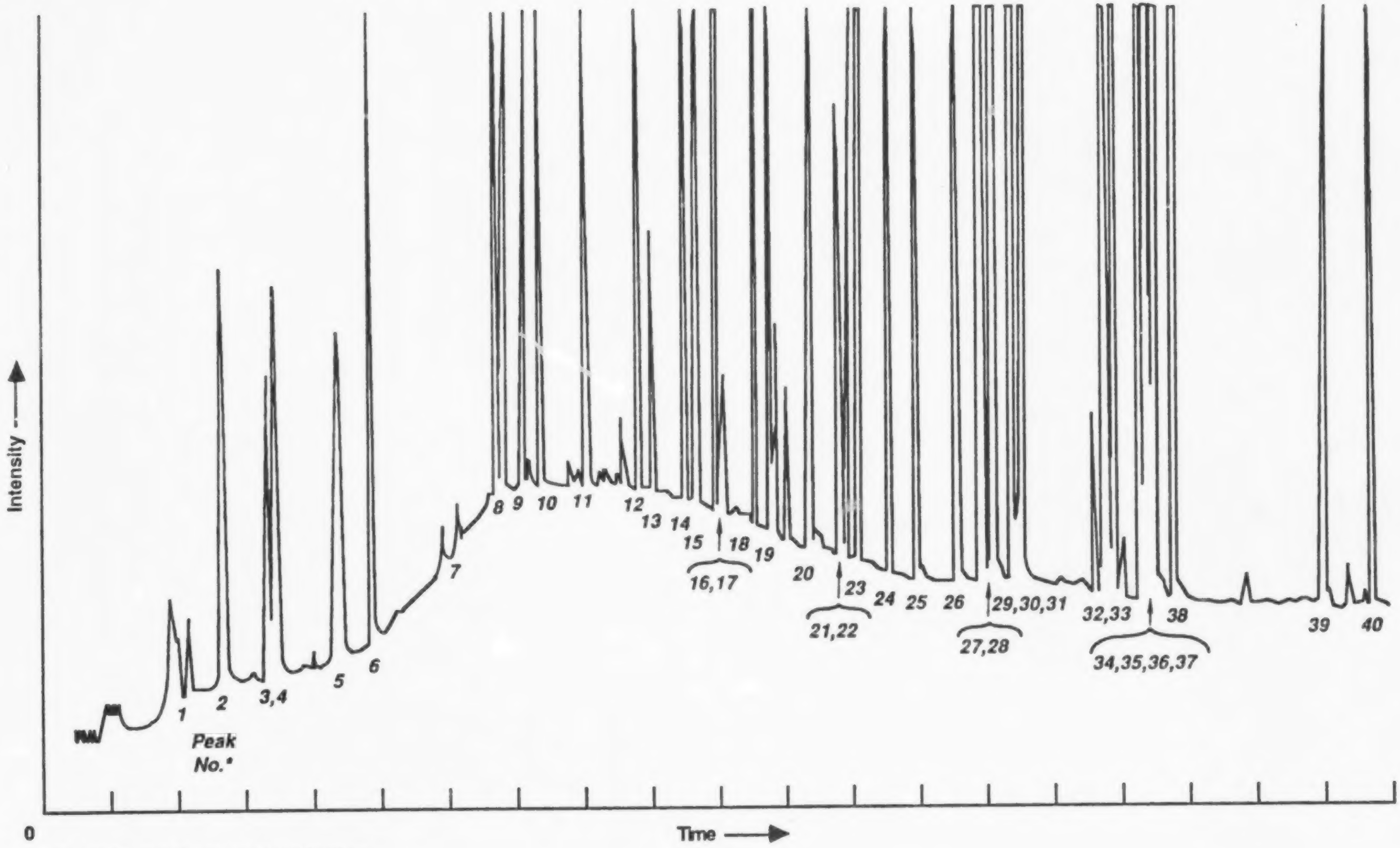
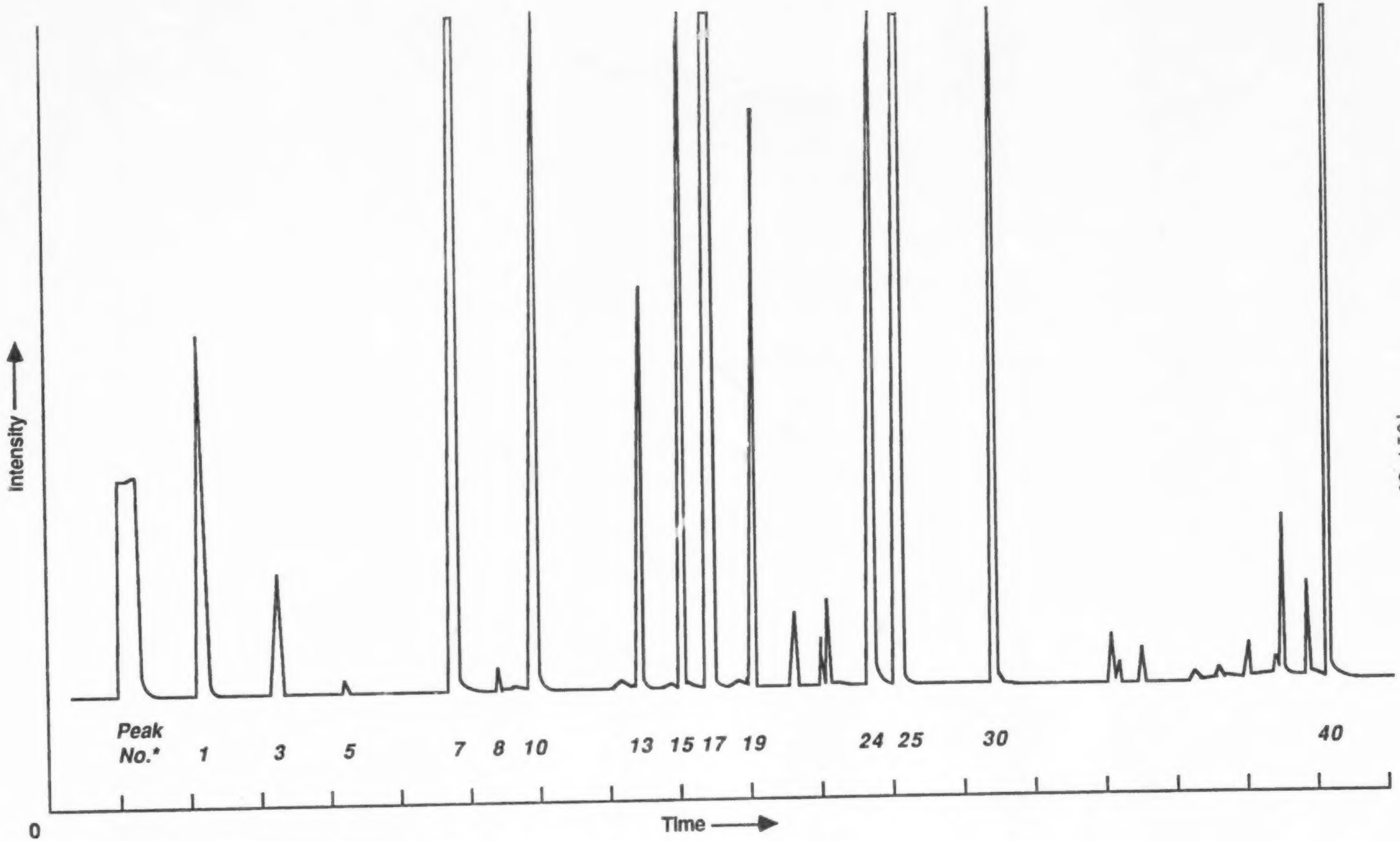

Receive
Sample
Canister
(Section
9.2.2)
Log Sample In
(Section 10.4.1.2)
Check and Record
Initial Pressure
(Section 10.4.1.3)
< 83 kPa
(12 psig)
(Optional)
Pressurize with N2
To 138 kPa
(20 psig)
Record Final Pressure
(Section 10.4.1.5)
Calculate Dilution Factor
(Section 10.4.1.4)
Analyze
Preparation of GC-FID-ECD-PID
Analytical System
Initial Preparation
Routine Preparation
Humid Zero Air Test and
Retention Time Window Test
Initial Three (3) Point
Static Calibration
Additional Five (5) Point Static
Calibration for Nonlinear Compounds
External
Standard
Calibration
Humid Zero Air Test and
Retention Time Window Test
Daily One (1) Point
Static Calibration
Additional Three (3) Point Static
Calibration for Nonlinear Compounds
GC-FID-ECD-PID
Analysis for Primary Quantitation

FIGURE 14. FLOWCHART OF GC-FID-ECD-PID ANALYTICAL SYSTEM PREPARATION



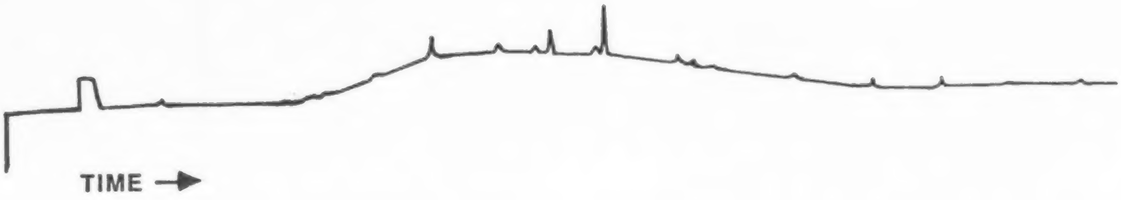
* See Table 7.0 For Peak Identification

FIGURE 15. TYPICAL FID RESPONSE TO SELECTIVE VOCs

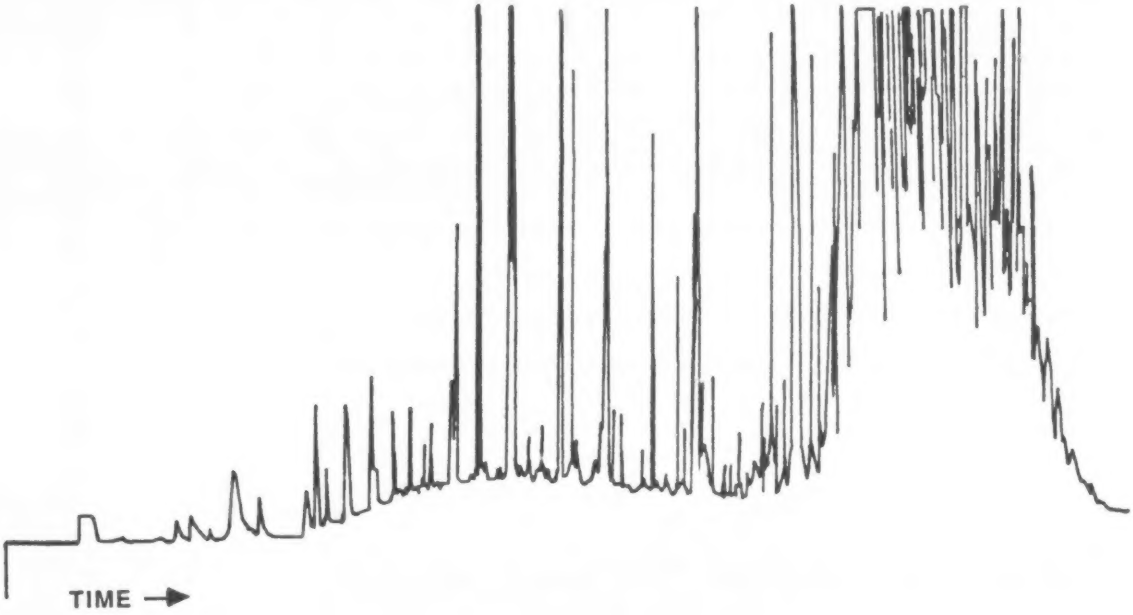


* See Table 7.0 For Peak Identification

FIGURE 16. TYPICAL ECD RESPONSE TO SELECTIVE VOCs



(a). Certified Sampler



(b). Contaminated Sampler

FIGURE 17. EXAMPLE OF HUMID ZERO AIR TEST RESULTS FOR A CLEAN SAMPLER (a) AND A CONTAMINATED SAMPLER (b)

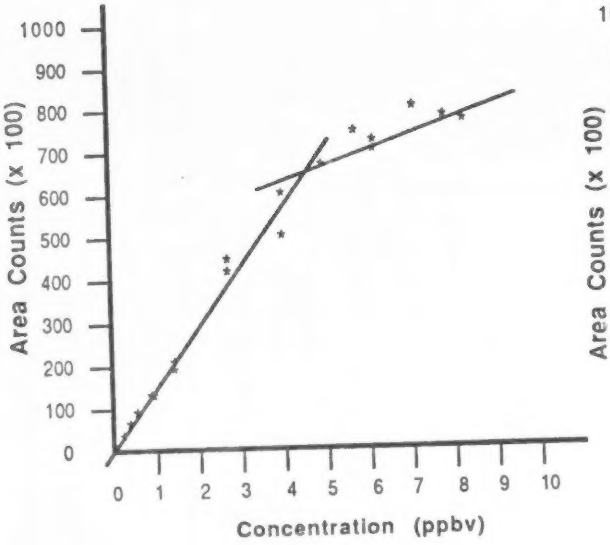


FIGURE 18(a). NONLINEAR RESPONSE OF TETRACHLOROETHYLENE ON THE ECD

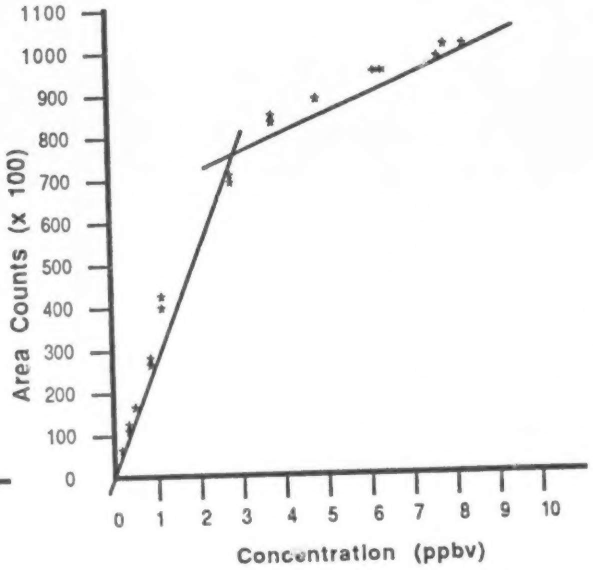


FIGURE 18(b). NONLINEAR RESPONSE OF CARBON TETRACHLORIDE ON THE ECD

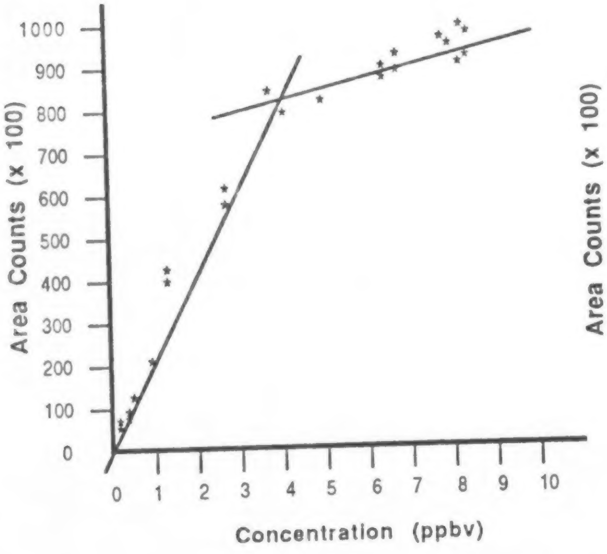


FIGURE 18(c). NONLINEAR RESPONSE OF HEXACHLOROBUTADIENE ON THE ECD

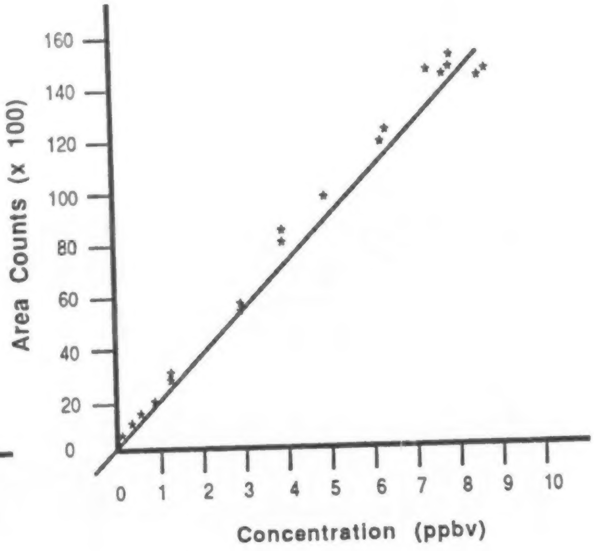


FIGURE 18(d). LINEAR RESPONSE OF CHLOROFORM ON THE ECD

FIGURE 18. RESPONSE OF ECD TO VARIOUS VOCs

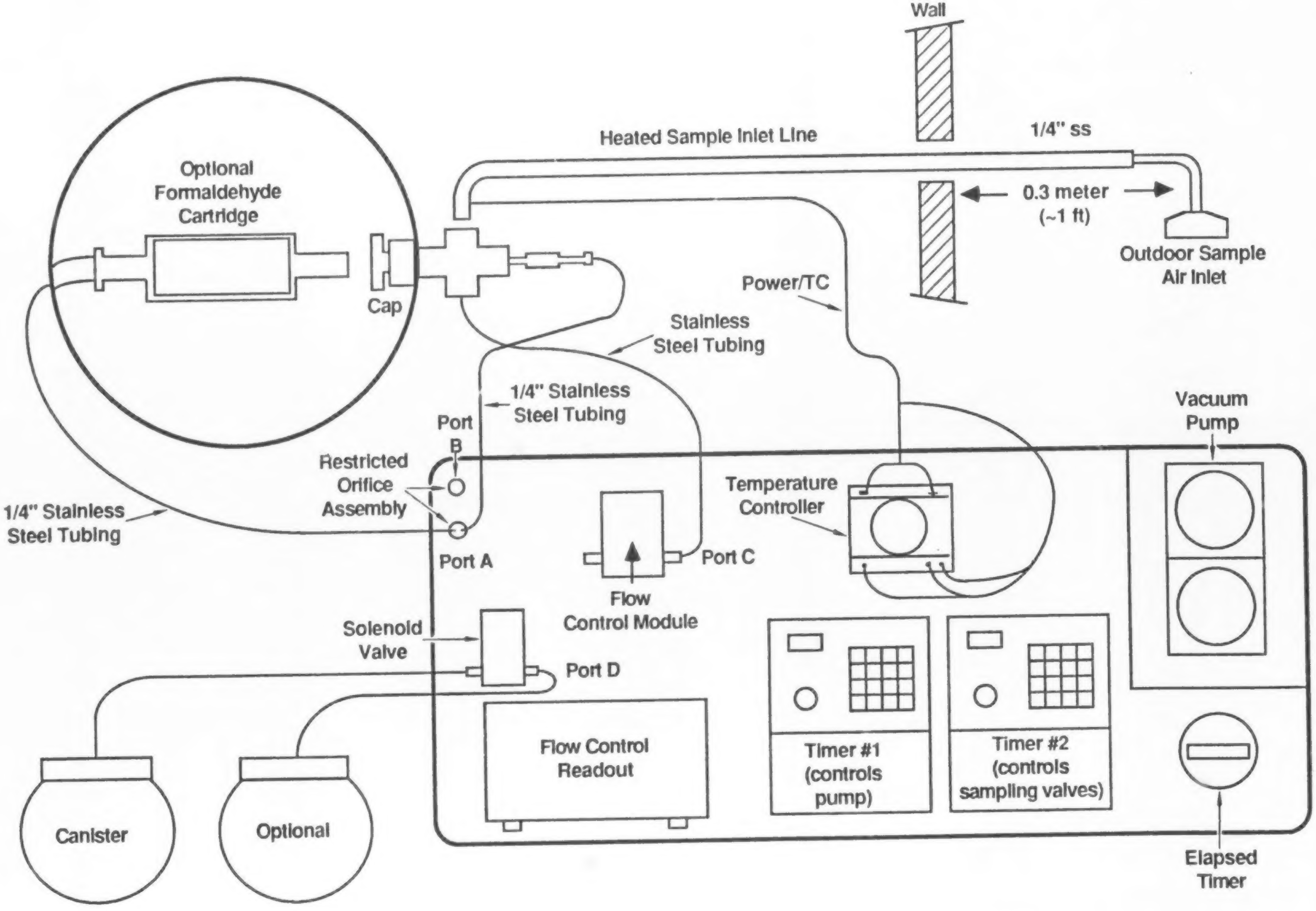

Wall
Heated Sample Inlet Line
1/4" ss
0.3 meter
(~1 ft)
Outdoor Sample
Air Inlet
Optional
Formaldehyde
Cartridge
Cap
Power/TC
Stainless
Steel Tubing
1/4" Stainless
Steel Tubing
Vacuum
Pump
Port
B
Restricted
Orifice
Assembly
Temperature
Controller
1/4" Stainless
Steel Tubing
Port A
Port C
Flow
Control Module
Solenoid
Valve
Port D
Flow Control
Readout
Timer #1
(controls
pump)
Timer #2
(controls
sampling valves)
Canister
Optional
Elapsed
Timer

FIGURE 19. U.S. ENVIRONMENTAL PROTECTION AGENCY UATP, SCHEMATIC OF SAMPLE INLET CONNECTIONS SAMPLER

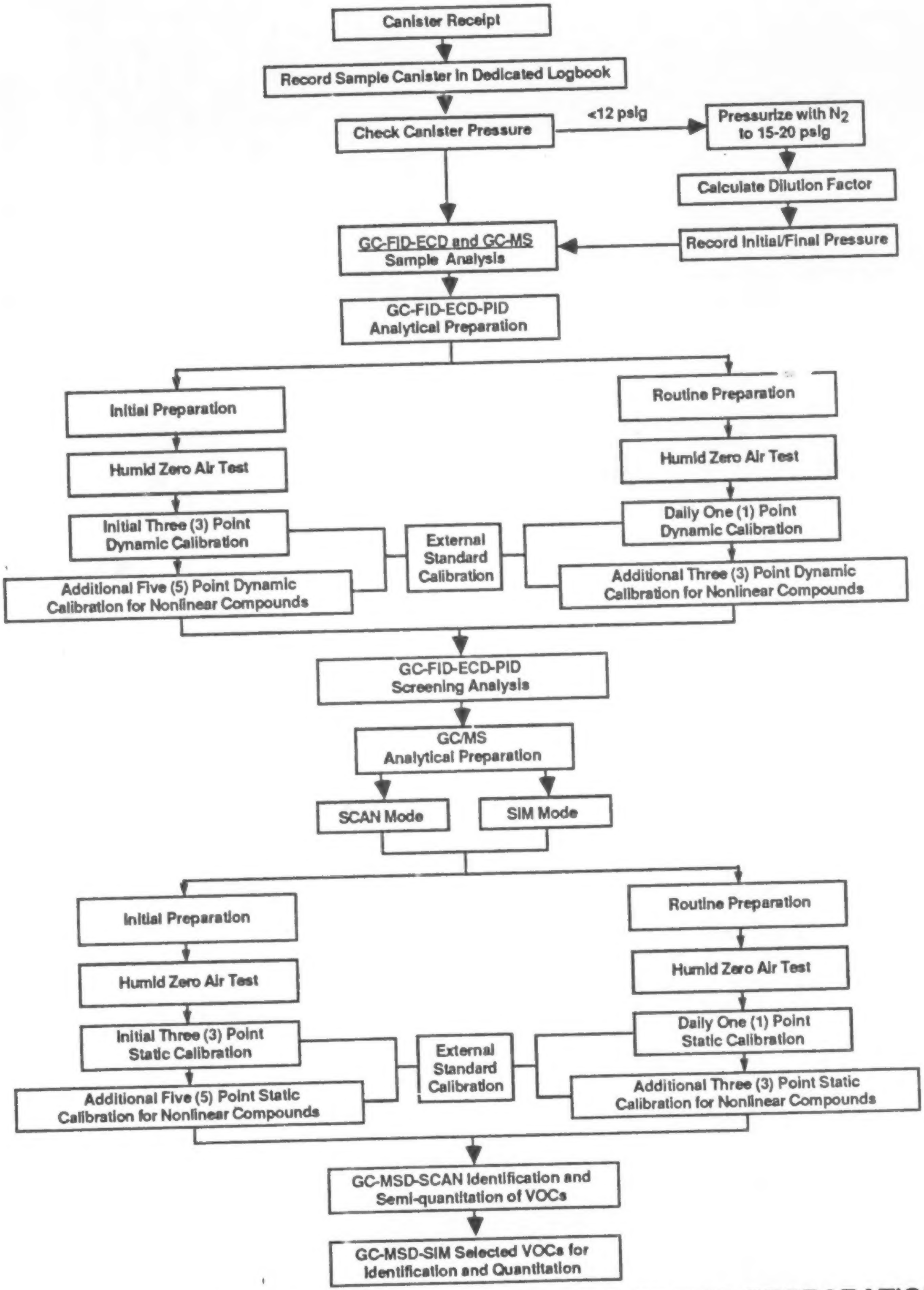

Canister Receipt
Record Sample Canister In Dedicated Logbook
Check Canister Pressure
<12 psig
Pressurize with N_2 to 15-20 psig
Calculate Dilution Factor
Record Initial/Final Pressure
GC-FID-ECD and GC-MS Sample Analysis
GC-FID-ECD-PID Analytical Preparation
Initial Preparation
Humid Zero Air Test
Initial Three (3) Point Dynamic Calibration
Additional Five (5) Point Dynamic Calibration for Nonlinear Compounds
External Standard Calibration
Routine Preparation
Humid Zero Air Test
Daily One (1) Point Dynamic Calibration
Additional Three (3) Point Dynamic Calibration for Nonlinear Compounds
GC-FID-ECD-PID Screening Analysis
GC/MS Analytical Preparation
SCAN Mode
SIM Mode
Initial Preparation
Humid Zero Air Test
Initial Three (3) Point Static Calibration
Additional Five (5) Point Static Calibration for Nonlinear Compounds
External Standard Calibration
Routine Preparation
Humid Zero Air Test
Daily One (1) Point Static Calibration
Additional Three (3) Point Static Calibration for Nonlinear Compounds
GC-MSD-SCAN Identification and Semi-quantitation of VOCs
GC-MSD-SIM Selected VOCs for Identification and Quantitation

FIGURE 20. FLOWCHART OF ANALYTICAL SYSTEMS PREPARATION.

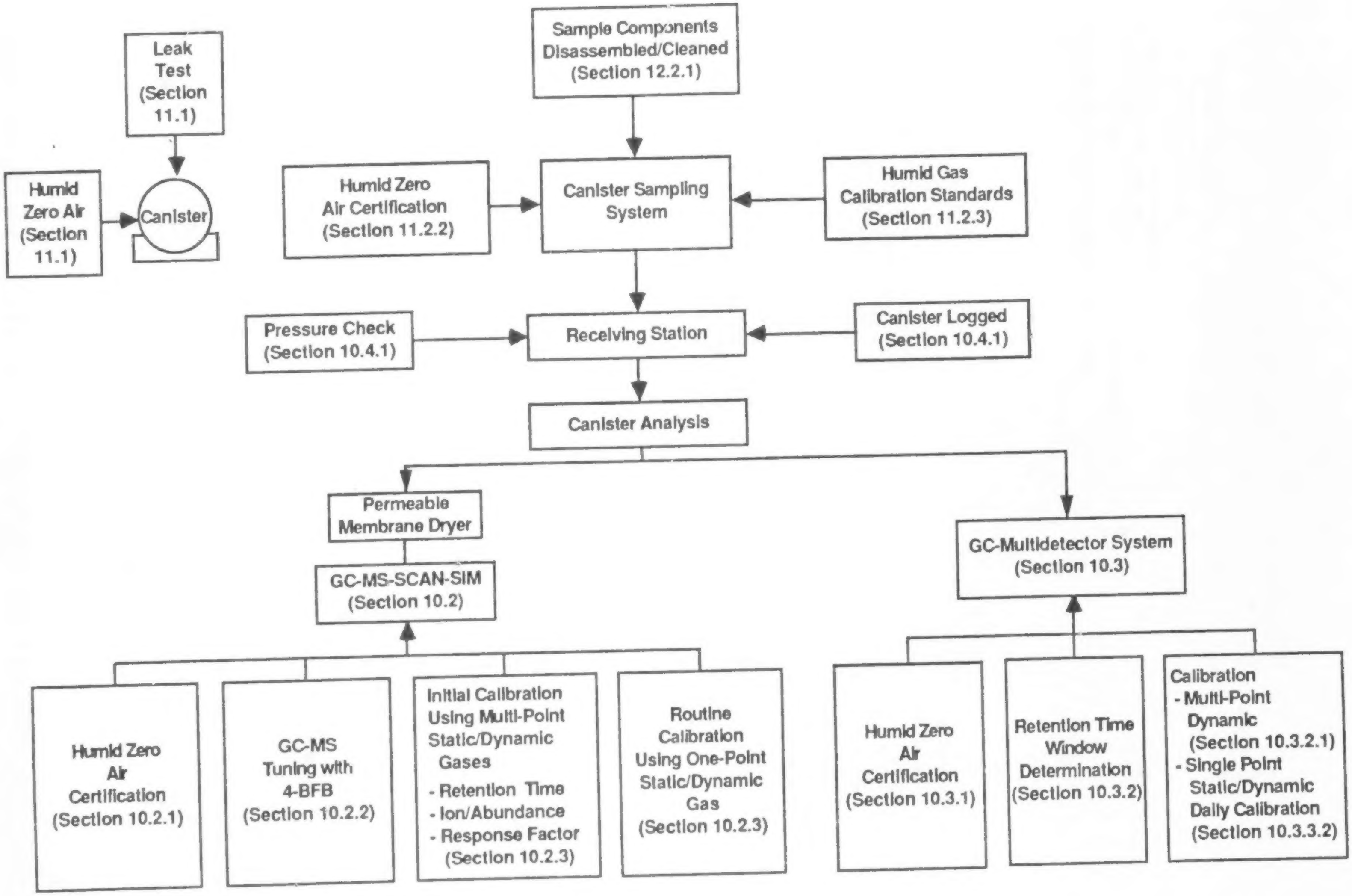

Leak Test (Section 11.1)
Humid Zero Air (Section 11.1)
Canister
Sample Components Disassembled/Cleaned (Section 12.2.1)
Humid Zero Air Certification (Section 11.2.2)
Canister Sampling System
Humid Gas Calibration Standards (Section 11.2.3)
Pressure Check (Section 10.4.1)
Receiving Station
Canister Logged (Section 10.4.1)
Canister Analysis
Permeable Membrane Dryer
GC-MS-SCAN-SIM (Section 10.2)
GC-Multidetector System (Section 10.3)
Humid Zero Air Certification (Section 10.2.1)
GC-MS Tuning with 4-BFB (Section 10.2.2)
Initial Calibration Using Multi-Point Static/Dynamic Gases
- Retention Time
- Ion/Abundance
- Response Factor
(Section 10.2.3)
Routine Calibration Using One-Point Static/Dynamic Gas (Section 10.2.3)
Humid Zero Air Certification (Section 10.3.1)
Retention Time Window Determination (Section 10.3.2)
Calibration
- Multi-Point Dynamic (Section 10.3.2.1)
- Single Point Static/Dynamic Daily Calibration (Section 10.3.3.2)

FIGURE 21. SYSTEM QUALITY ASSURANCE / QUALITY CONTROL (QA/QC) ACTIVITIES ASSOCIATED WITH VARIOUS ANALYTICAL SYSTEMS

APPENDIX A

AVAILABILITY OF AUDIT CYLINDERS FROM UNITED STATES ENVIRONMENTAL PROTECTION AGENCY USEPA PROGRAMS/ REGIONAL OFFICES, STATE AND LOCAL AGENCIES AND THEIR CONTRACTORS

1. Availability of Audit Cylinders

1.1 The USEPA has available, at no charge, cylinder gas standards of hazardous organic compounds at the ppb level that may be used to audit the performance of ambient air source measurement systems.

1.2 Each audit cylinder contains 5 to 18 hazardous organic compounds in a balance of N_2 gas. Audit cylinders are available in several concentration ranges. The concentration of each organic compound in the audit cylinder is within the range illustrated in Table A-1.

2. Audit Cylinder Certification

2.1 All audit cylinders are periodically analyzed to assure that cylinder concentrations have remained stable.

2.2 All stability analyses include quality control analyses of ppb hazardous organic gas standards prepared by the National Bureau of Standards for USEPA.

3. Audit Cylinder Acquisition

3.1 USEPA program/regional offices, state/local agencies, and their contractors may obtain audit cylinders (and an audit gas delivery system, if applicable) for performance audits during:

- o RCRA Hazardous Waste Trial Burns For PHOC's; and
- o Ambient Air Measurement of Toxic Organics.

3.2 The audit cylinders may be acquired by contacting:

Robert L. Lampe
U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division
MD-77B
Research Triangle Park, NC 27711
919-541-4531

TABLE A-1. AVAILABLE USEPA PERFORMANCE AUDIT CYLINDERS

Group I Compounds	Group II Compounds	Group III Compounds
Carbon tetrachloride	Trichloroethylene	Pyridine (Pyridine in Group III cylinders but certified analysis not available)
Chloroform	1,2-dichloroethane	Vinylidene chloride
Perchloroethylene	1,2-dibromoethane	1,1,2-trichloro-1,2,2-trifluoroethane (Freon-113)
Vinyl chloride	Acetonitrile	1,2-dichloro-1,1,2,2-tetrafluoroethane (Freon-114)
Benzene	Trichlorofluoromethane (Freon-11)	Acetone
	Dichlorodifluoromethane (Freon-12)	1-4 Dioxane
	Bromomethane	Toluene
	Methyl ethyl ketone	Chlorobenzene
	1,1,1-trichloroethane	

Group I Ranges	Group II Ranges	Group III Ranges
7 to 90 ppb	7 to 90 ppb	7 to 90 ppb
90 to 430 ppb	90 to 430 ppb	90 to 430 ppb
430 to 10,000 ppb		

Group IV	Group V	
Acrylonitrile	Carbon tetrachloride	Methylene chloride
1,3-butadiene	Chloroform	Trichlorofluoromethane (Freon-11)
Ethylene oxide	Perchloroethylene	Bromomethane
Methylene chloride	Vinyl chloride	Toluene
Propylene oxide	Benzene	Chlorobenzene
o-xylene	Trichloroethylene	1,3-Butadiene
	1,2-dichloroethane	o-xylene
	1,2-dibromoethane	Ethyl benzene
	1,1,1-trichloroehtane	1,2-dichloropropane

Group IV Ranges	Group V Ranges
7 to 90 ppb	1 to 40 ppb
430 to 10,000 ppb	

APPENDIX B I

OPERATING PROCEDURES FOR A PORTABLE GAS CHROMATOGRAPH EQUIPPED WITH A PHOTOIONIZATION DETECTOR

1. Scope

This procedure is intended to screen ambient air environments for volatile organic compounds. Screening is accomplished by collection of VOC samples within an area and analysis on site using a portable gas chromatograph/integrator (Photovac Models 10S10, 10S50, or equivalent). This procedure is not intended to yield quantitative or definite qualitative information regarding the substances detected. Rather, it provides a chromatographic "profile" of the occurrence and intensity of unknown volatile compounds which assists in placement of fixed-site samplers.

2. Applicable Documents

2.1 ASTM Standards

E260 - Recommended Practice for General Gas Chromatography Procedures

E355 - Practice for Gas Chromatography Terms and Relationships

2.2 Other Documents

Portable Instruments User's Manual for Monitoring VOC Sources, EPA-34011-86-015, U.S. Environmental Protection Agency, Washington, DC, June, 1986.

3. Summary of Method

3.1 An air sample is extracted directly from ambient air and analyzed on site by a portable GC.

3.2 Analysis is accomplished by drawing an accurate volume of ambient air through a sampling port and into a concentrator, then the sample air is transported by carrier gas onto a packed column and into a PID, resulting in response peak(s). Retention times are compared with those in a standard chromatogram to predict the probable identity of the sample components.

4. Significance

4.1 VOCs are emitted into the atmosphere from a variety of sources including petroleum refineries, synthetic organic chemical plants, natural gas processing plants, and automobile exhaust. Many of these VOC emissions are acutely toxic; therefore, their determination in ambient air is necessary to assess human health impacts.

4.2 Conventional methods for VOC determination use solid sorbent and canister sampling techniques.

4.3 Collection of ambient air samples in canisters provides (1) convenient integration of ambient samples over a specific time period, (e.g., 24 hours); (2) remote sampling and central analysis; (3) ease of storing and shipping samples, if necessary; (4) unattended sample collection; (5) analysis of samples from multiple sites with one analytical system; and (6) collection of sufficient sample volume to allow assessment of measurement precision and/or analysis of samples by several analytical systems.

4.4 The use of portable GC equipped with multidetectors has assisted air toxics programs by using the portable GC as a "screening tool" to determine "hot spots," potential interferences, and semi-quantitation of VOCs/SVOCs, prior to locating more traditional fixed-site samplers.

5. Definitions

Definitions used in this document and in any user-prepared Standard Operating Procedures (SOPs) should be consistent with ASTM Methods D1356 and E355. Abbreviations and symbols pertinent to this method are defined at point of use.

6. Interferences

6.1 The most significant interferences result from extreme differences in limits of detection (LOD) among the target VOCs (Table B-1). Limitations in resolution associated with ambient temperature, chromatography and the relatively large number of chemicals result in coelution of many of the target components. Coelution of compounds with significantly different PID sensitivities will mask compounds with more modest sensitivities. This will be most dramatic in interferences from benzene and toluene.

6.2 A typical chromatogram and peak assignments of a standard mixture of target VOCs (under the prescribed analytical conditions of this method) are illustrated in Figure B-1. Samples which contain a highly complex mixture of components and/or interfering levels of benzene and toluene are analyzed on a second, longer chromatographic column. The same liquid phase in the primary column is contained in the alternate column but at a higher percent loading.

6.3 Recent designs in commercially available GCs (Table B-2) have pre-concentrator capabilities for sampling lower concentrations of VOCs, pre-column detection with back-flush capability for shorter analytical time, constant column temperature for method precision and accuracy and multidetector (PID, ECD, and FID) capability for versatility. Many of these newer features address the weaknesses and interferences mentioned above.

7. Apparatus

7.1 Gas chromatograph. A GC (Photovac Inc., 739 B Parks Ave, Huntington, NY, 11743, Model 10S10 or 10S50, or equivalent) used for surveying ambient air environments (which could employ a multidetector) for sensing numerous VOCs compounds eluting from a packed column at ambient temperatures. This particular portable GC procedure is written employing the photoionization detector as its major sensing device, as part of the Photovac Model 10S10 portable GC survey tool. Chromatograms are developed on a column of 3% SP-2100 on 100/120 Supelcoport (0.66 m x 3.2 mm I.D.) with a flow of 30 cm^3/min air.

7.2 GC accessories. In addition to the basic gas chromatograph, several other pieces of equipment are required to execute the survey sampling. Those include gas-tight syringes for standard injection, alternate carrier gas supplies, high pressure connections for filling the internal carrier gas reservoir, and if the Model 10S10 is used, a recording integrator (Hewlett Packard, Avondale, PA, Model 3390A, or equivalent).

8. Reagents and Materials

8.1 Carrier gas. "Zero" air [<0.1 ppm total hydrocarbon (THC)] is used as the carrier gas. This gas is conveniently contained in 0.84 m^3 (30 ft^3) aluminum cylinders. Carrier gas of poorer quality may result in spurious peaks in sample chromatograms. A Brooks, Type 1355-00F1AAA rotameter (or equivalent) with an R-215-AAA tube and glass float is used to set column flow.

8.2 System performance mixture. A mixture of three target compounds (e.g., benzene, trichloroethylene, and styrene) in nitrogen is used for monitoring instrument performance. The approximate concentration for each of the compounds in this mixture is 10 parts per billion (ppb). This mixture is manufactured in small, disposable gas cylinders [at 275 kPa (40 psi)] from Scott Specialty Gases, or equivalent.

8.3 Reagent grade nitrogen gas. A small disposable cylinder of high purity nitrogen gas is used for blank injections.

8.4 Sampling syringes. Gas-tight syringes, without attached shut-off valves (Hamilton Model 1002LT, or equivalent) are used to introduce accurate sample volumes into the high pressure injectors on the portable gas chromatograph. Gas syringes with shut-off valves are not recommended because of memory problems associated with the valves. For samples suspected of containing high concentrations of volatile compounds, disposable glass syringes (e.g, Glaspak, or equivalent) with stainless steel/Teflon® hub needles are used.

8.5 High pressure filler. An adapter (Photovac SA101, or equivalent) for filling the internal carrier gas reservoir on the portable GC is used to deliver "zero" air.

9. Procedure

9.1 Instrument Setup

9.1.1 The portable gas chromatograph must be prepared prior to use in the ambient survey sampling. The pre-sampling activities consist of filling the internal carrier gas cylinder, charging the internal power supply, adjusting individual column carrier gas flows, and stabilizing the photoionization detector.

9.1.2 The internal reservoir is filled with "zero" air. The internal 12V, 6AH lead/acid battery can be recharged to provide up to eight hours of operation. A battery which is discharged will automatically cause the power to the instrument to be shut down and will require an overnight charge. During AC operation, the batteries will automatically be trickle-charged or in a standby mode.

9.1.3 The portable GC should be operated (using the internal battery power supply) at least forty minutes prior to collection of the first sample to insure that the photoionzation detector has stabilized. Upon arriving at the area to be sampled, the unit should be connected to AC power, if available.

9.2 Sample Collection

9.2.1 After the portable gas chromatograph is located and connected to 110V AC, the carrier gas flows must be adjusted. Flows to the 1.22 meter, 5% SE-30 and 0.66 meter, 3% SP2100 columns are adjusted with needle valves. Flows of 60 cm^3/min (5% SE-30) and 30 cm^3/min (3% SP2100) are adjusted by means of a calibrated rotameter. Switching between the two columns is accomplished by turning the valve located beneath the electronic module. During long periods of inactivity, the flows to both columns should be reduced to conserve pressure in the internal carrier gas supply. The baseline on the recorder/integrator is set to 20% full scale.

9.2.2 Prior to analysis of actual samples, an injection of the performance evaluation mixture must be made to verify chromatographic and detector performance. This is accomplished by withdrawing 1.0 mL samples of this mixture from the calibration cylinder and injecting it onto the 3% SP2100 column. The next sample analyzed should be a blank, consisting of reagent grade nitrogen.

9.2.3 Ambient air samples are injected onto the 3% SP2100 column. The chromatogram is developed for 15 minutes. Samples which produce particularly complex chromatograms, especially for early eluting components, are reinjected on the 5% SE-30 column. [Note: In no instance should a syringe which has been used for the injection of the calibrant/system performance mixture be used for the acquisition and collection of samples, or vice versa.]

9.2.4 Samples have generally been collected from the ambient air at sites which are near suspected sources of VOCs and SVOCs and compared with those which are not. Typically, selection of sample locations is based on the presence of chemical odors. Samples collected in areas without detectable odors have not shown significant PID responses. Therefore, sampling efforts should be initially concentrated on "suspect" environments (i.e., those which have appreciable odors). The objective of the sampling is to locate sources of the target compounds. Ultimately, samples should be collected throughout the entire location, but with particular attention given to areas of high or frequent occupation.

9.3 Sample Analysis

9.3.1 Qualitative analysis. Positive identification of sample components is not the objective of this "screening" procedure. Visual comparison of retention times to those in a standard chromatogram (Figure B-1) are used only to predict the probable sample component types.

9.3.2 Estimation of levels. As with qualitative analysis, estimates of component concentrations are extremely tentative and are based on instrument responses to the calibrant species (e.g., benzene, trichloroethylene, styrene), the proposed component identification, and the difference in response between sample component and calibrant. For purposes of locating pollutant emission sources, roughly estimated concentrations and suspected compound types are considered sufficient.

10. Performance Criteria and Quality Assurance

Required quality assurance measures and guidance concerning performance criteria that should be achieved within each laboratory are summarized and provided in the following section.

10.1 Standard Operating Procedures

10.1.1 SOPs should be generated by the users to describe and document the following activities in their laboratory: (1) assembly, calibration, leak check, and operation of the specific portable GC sampling system and equipment used; (2) preparation, storage, shipment, and handling of the portable GC sampler; (3) purchase, certification, and transport of standard reference materials; and (4) all aspects of data recording and processing, including lists of computer hardware and software used.

10.1.2 Specific stepwise instructions should be provided in the SOPs and should be readily available to and understood by the personnel conducting the survey work.

10.2 Quality Assurance Program

10.2.1 Reagent and materials control. The carrier gas employed with the portable GC is "zero air" containing less than 0.1 ppm VOCs. System performance mixtures are certified standard mixtures purchased from Scott Specialty Gases, or equivalent.

10.2.2 Sampling protocol and chain of custody. Sampling protocol sheets must be completed for each sample. Specifics of the sample with regard to sampling location, sample volume, analysis conditions, and supporting calibration and visual inspection information are detailed by these documents. An example form is exhibited in Table B-3.

10.2.3 Blanks, Duplicates, and System Performance Samples

10.2.3.1 Blanks and Duplicates. Ten percent of all injections made to the portable GC are blanks, where the blank is reagent grade nitrogen gas. This is the second injection in each sampling location. An additional 10% of all injections made are duplicate injections. This will enhance the probability that the chromatogram of a sample reflects only the composition of that sample and not any previous injection. Blank injections showing a significant amount of contaminants will be cause for remedial action.

10.2.3.2 System Performance Mixture. An injection of the system performance mixture will be made at the beginning of a visit to a particular sampling location (i.e., the first injection). The range of acceptable chromatographic system performance criteria and detector response is shown in Table B-4. These criteria are selected with regard to the intended application of this protocol and the limited availability of standard mixtures in this area. Corrective action should be taken with the column or PID before sample injections are made if the performance is deemed out-of-range. Under this regimen of blanks and system performance samples, approximately eight samples can be collected and analyzed in a three hour visit to each sampling location.

10.3 Method Precision and Accuracy

The purpose of the analytical approach outlined in this method is to provide presumptive information regarding the presence of selected VOCs and SVOCs emissions. In this context, precision and accuracy are to be determined. However, quality assurance criteria are described in Section 10.2 which insure the samples collected represent the ambient environment.

10.4 Range and Limits of Detection

The range and limits of detection of this method are highly compound dependent due to large differences in response of the portable GCs photoionization detector to the various target compounds. Aromatic compounds and olefinic halogenated compounds will be detected at lower levels than the halomethanes or aliphatic hydrocarbons. The concentration range of application of this method is approximately two orders of magnitude.

TABLE B-1

ESTIMATED LIMITS OF DETECTION (LOD) FOR SELECTED VOCs BASED ON 1 uL SAMPLE VOLUME

Compound	LOD (ng)	LOD (ppb)
Chloroform[a]	2	450
1,1,1-Trichloroethane[a]	2	450
Carbon tetrachloride[a]	2	450
Benzene	.006	2
1,2-Dichloroethane[b]	.05	14
Trichloroethylene[b]	.05	14
Tetrachloroethylene[b]	.05	14
1,2-Dibromoethane	.02	2
p-Xylene[c]	.02	4
m-Xylene[c]	.02	4
o-Xylene[d]	.01	3
Styrene[d]	.01	3

[a] Chloroform, 1,1,1-Trichloroethane, and Carbon tetrachloride coelute on 0.66 m 3% SP2100.

[b] 1,2-Dichloroethane, Tricholroethylene, and Tetrachloroethylene coelute on 0.66 m 3% SP2100.

[c] p-Xylene and m-Xylene coelute on 0.66 m 3% SP2100.

[d] Styrene and o-Xylene coelute on 0.66 m 3% SP2100.

TABLE B-2

COMMERCIALLY AVAILABLE PORTABLE VOC DETECTION INSTRUMENTS

Monitor	Detection principle	Range, ppm	Sensitivity	Response time, s	Accessories	Calibration Techniques	Weaknesses	Service Rate	Lack of Response	Cost,$	Samp Rate L/m
550,551 555,580 (AID, Inc.	PID, FID	0-200, 0-2000, 0-10,000	0.1 ppm at 0-200 ppm	<5		o Bag Sampling	o Umbilical cord too short o Digital readout hard to read o Flame out frequently	8 hrs		4,300	1.5
OVA 108, 128 Century Systems, Inc. (Foxboro)	FID	0-10, 0-100, 0-1000, 0-10,000, 0-100,000	0.2 ppm (Model 128) 0.5 ppm (Model 108)	2 2	o Thermal Desorbers available o Optional GC available	o Hand Space o Direct Injection o Bag Samp.	o Battery failure o Sample line kinks o Compounds containing O_2/N give low response o Neg. resp. to CO/CO_2	8 hrs		6,300	
PI-101 (HNu Systems, Inc)	PID	1 1-20 1-200 1-2000	0.1 ppm Low molecular weights aromatics	<5	o Three lamps available o 9.5 (aromatics) o 10.2 (2-4 compounds) o 11.7 (halocarbons)	o External Gas Cyl. o Bag Samp.	o Three lamps - may miss something	10 hrs	o C1 hydro carbons o CH_4	4,955	0.5
TLV Sniffer (Bacharach)	Catalytic combustion	0-500 0-5000 0-50,000	2.0 ppm	5		o Bag Samp. o Head Space				900	
Ecolyzer 400 (Energetics Science)	Catalytic combustion	0-100% LFL	1% LFL	15		o Bag Samp.	o Changes in gas temp/humidity affects response				
Miran 1A (Foxboro)	IR	ppm to %	1 ppm	1,4,10 and 40						9,500	
Miran 1B (Foxboro)	IR	ppm to %								12,500	
Scentor (Sentex)	GC/EC, Argon Ionization PID		0.01 ppb Cl organics	2	Preconcentrator Thermal Desoprtion GC Columns Auto Cal. from Integral Gas Cylinder	o Internal gas cyl. o Preconcentrator o GC Column				12,950	
Photovac Standard Automatic Computer Auto Comp. Communication	PID (UV Light)	0	0.1 ppb Benzene with signal-to-noise ratio 4:1, Good for aromatics	2	o Dual Column o Manual/Auto Injection o Column Cond. o Pre-flush o Auto Dial Modem o Programmable		o Column operates at ambient temp. o STD in lab, then to field at diff. temp o Can't inject liquid samp. o Light fractions interfere		o H_2O o O_2	6,995 8,995 10,500 10,955 12,955	
Photovac Tip	PID	0-2000 ppm	0.05 ppm Benzene	3							

TABLE B-3

PORTABLE GAS CHROMATOGRAPH SAMPLING DATA SHEET

DATE: ______________ LOCATION: ______________ TIME: ________

CHROMATOGRAPHIC CONDITIONS: ______________________________

COLUMN 1: COLUMN TYPE:

I.D. (mm):________ LENGTH (mm):_______ FLOW (mL/min):________

COLUMN 2: COLUMN TYPE:

I.D. (mm):________ LENGTH (mm):_______ FLOW (mL/min):________

INJ. NO.	INJ. VOL.	COLUMN NO.	SETTING	LOCATION

SITE PLAN (indicate sampling locations):

________________ DATE

________________ SIGNATURE

TABLE B-4

SYSTEM PERFORMANCE CRITERIA FOR PORTABLE GC[a]

Criteria	Test Compound	Acceptable Range	Suggested Corrective Action
PID Response	Trichloroethylene	$\geq 10^8$ uV-sec/ng	Re-tune or replace lamp
Elution Time	Styrene	2.65 ± 0.15 min	Inspect for leaks, adjust carrier flow
Resolution[b]	Benzene/Trichloroethylene	≥ 1.4	Replace column

[a] Based on analysis of a vapor mixture of benzene, styrene, and trichloroethylene.

[b] Define by: $R + = 2d/(W_1+W_2)$; where d = distance between the peaks and W = peak width at base.

TABLE B-5

ESTIMATED LIMITS OF DETECTION (LOD) FOR SELECTED VOCs

Compound	LOD (ng)	LOD (ppb)
Chloroform[a]	2	450
1,1,1-Trichloroethane[a]	2	450
Carbon tetrachloride[a]	2	450
Benzene	.006	2
1,2-Dichloroethane[b]	.05	14
Trichloroethylene[b]	.05	14
Tetrachloroethylene[b]	.05	14
1,2-Dibromoethane	.02	2
p-Xylene[c]	.02	4
m-Xylene[c]	.02	4
o-Xylene[d]	.01	3
Styrene[d]	.01	3

[a] Chloroform, 1,1,1-Trichloroethane, and Carbon tetrachloride coelute on 0.66 m 3% SP2100.

[b] 1,2-Dichloroethane, Trichloroethylene, and Tetrachloroethylene coelute on 0.66 m 3% SP2100.

[c] p-Xylene and m-Xylene coelute on 0.66 m 3% SP2100.

[d] Styrene and o-Xylene coelute on 0.66 m 3% SP2100.

Peak Assignments For Standard Mixture

Peak No.	Compound(s)[a]
1	Benzene; Chloroform; 1,1,1-Trichloroethane; Carbon Tetrachloride
2	1,2-Dichloroethane; Trichloroethylene
3	Tetrachloroethylene; 1,2-Dibromoethane
4	Ethylbenzene
5	m,p- Xylene
6	o- Xylene; Styrene

[a] Toluene (not listed) elutes between peaks 1 and 2.

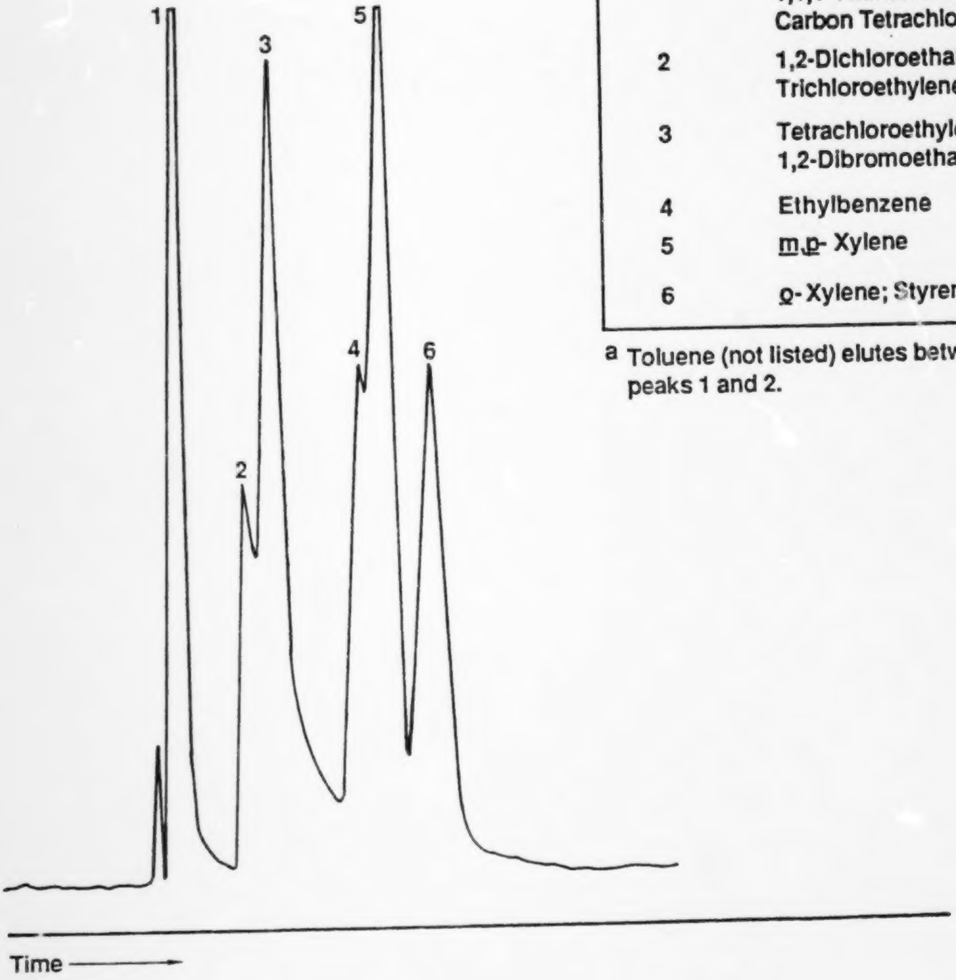


FIGURE B-1. TYPICAL CHROMATOGRAM OF VOCs DETERMINED BY A PORTABLE GC

APPENDIX C

INSTALLATION AND OPERATION PROCEDURES FOR U.S. ENVIRONMENTAL PROTECTION AGENCY'S URBAN AIR TOXIC POLLUTANT PROGRAM SAMPLER

1. Scope

1.1 The subatmospheric sampling system described in this method has been modified and redesigned specifically for use in USEPA's Urban Air Toxic Pollutant Program (UATP), a joint project of USEPA's Office of Air Quality Planning and Standards, the Environmental Monitoring Systems Laboratory, and the participating state air pollution control agencies. The purpose of UATP is to provide analytical support to the states in their assessment of potential health risks from certain toxic organic compounds that may be present in urban atmospheres. The sampler is described in the paper, "Automatic Sampler for Collection of 24-Hour Integrated Whole-Air Samples for Organic Analysis," to be presented at the 1988 Annual Meeting of APCA, Dallas, Texas, June, 1988 (Paper No. 88-150.3).

1.2 The sampler is based on the collection of whole air samples in 6-liter, SUMMA® passivated stainless steel canisters. The sampler features electronic timer for ease, accuracy and flexibility of sample period programming, an independently setable presample warm-up and ambient air purge period, protection from loss of sample due to power interruptions, and a self-contained configuration housed in an all-metal portable case, as illustrated in Figure C-1.

1.3 The design of the sampler is pumpless, using an evacuated canister to draw the ambient sample air into itself at a fixed flow rate (3-5 cm^3/min) controlled by an electronic mass flow controller. Because of the relatively low sample flow rates necessary for the integration periods, auxiliary flushing of the sample inlet line is provided by a small, general-purpose vacuum pump (not in contact with the sample air stream). Further, experience has shown that inlet lines and surfaces sometimes build up or accumulate substantial concentrations of organic materials under stagnant (zero flow rate) conditions. Therefore such lines and surfaces need to be purged and equilibrated to the sample air for some time prior to the beginning of the actual sample collection period. For this reason, the sampler includes dual timers, one of which is set to start the pump several hours prior to the specified start of the sample period to purge the inlet lines and surfaces. As illustrated in Figure C-1, sample air drawn into the canister passes through only four components: the heated inlet line, a 2-micron particulate filter, the electron flow controller, and the latching solenoid valve.

2. Summary of Method

2.1 In operation, timer 1 is set to start the pump about 6 hours before the scheduled sample period. The pump draws sample air in through the sample inlet and particulate filter to purge and equilibrate these components, at a flow rate limited by the capillary to approximately 100 cm^3/min. Timer 1 also energizes the heated inlet line to allow it to come up to its controlled temperature of 65 to 70 degrees C, and turns on the flow controller to allow it to stabilize. The pump draws additional sample air through the flow controller by way of the normally open port of the 3-way solenoid valve. This flow purges the flow controller and allows it to achieve a stable controlled flow at the specified sample flow rate prior to the sample period.

2.2 At the scheduled start of the sample period, timer 2 is set to activate both solenoid valves. When activated, the 3-way solenoid valve closes its normally open port to stop the flow controller purge flow and opens its normally closed port to start flow through the aldehyde sample cartridges. Simultaneously, the latching solenoid valve opens to start sample flow into the canister.

2.3 At the end of the sample period, timer 2 closes the latching solenoid valve to stop the sample flow and seal the sample in the canister and also de-energizes the pump, flow controller, 3-way solenoid, and heated inlet line. During operation, the pump and sampler are located external to the sampler. The 2.4 meter (8 foot) heated inlet line is installed through the outside wall, with most of its length outside and terminated externally with an inverted glass funnel to exclude precipitation. The indoor end is terminated in a stainless steel cross fitting to provide connections for the canister sample and the two optional formaldehyde cartridge samples.

3. Sampler Installation

3.1 The sampler must be operated indoors with the temperature between 20-32°C (68 to 90°F). The sampler case should be located conveniently on a table, shelf, or other flat surface. Access to a source of 115 vac line power (500 watts min) is also required. The pump is removed from the sampler case and located remotely from the sampler (connected with a 1/4 inch O.D. extension tubing and a suitable electrical extension cord).

3.2 Electrical Connections (Figure C-1)

3.2.1 The sampler cover is removed. The sampler is not plugged into the 115 vac power until all other electrical connections are completed.

3.2.2 The pump is plugged into its power connector (if not already connected) and the battery connectors are snapped onto the battery packs on the covers of both timers.

3.2.3 The sampler power plug is inserted into a 115 volts ac line grounded receptacle. The sampler must be grounded for operator safety. The electrical wires are routed and tied so they remain out of the way.

3.3 Pneumatic Connections

3.3.1 The length of 1/16 inch O.D. stainless steel tubing is connected from port A of the sampler (on the right side of the flow controller module) to the air inlet line.

3.3.2 The pump is connected to the sampler with 1/4 inch O.D. plastic tubing. This tubing may be up to 7 meters (20 feet) long. A short length of tubing is installed to reduce pump noise. All tubing is conveniently routed and, if necessary, tied in place.

4. Sampler Preparation

4.1 Canister

4.1.1 The sample canister is installed no more than 2 days before the scheduled sampling day.

4.1.2 With timer #1 ON, the flow controller is allowed to warm up for at least 15 minutes, longer if possible.

4.1.3 An evacuated canister is connected to one of the short lengths of 1/8 inch O.D. stainless steel tubing from port B (solenoid valve) of the sampler. The canister valve is left closed. The Swagelok fitting on the canister must not be cross-threaded. The connection is tightened snugly with a wrench.

4.1.4 The end of the other length of stainless steel tubing from port B (solenoid valve) is connected with a Swagelok plug.

4.1.5 If duplicate canisters are to be sampled, the plug is removed from the second 1/8 inch O.D. stainless steel tubing from port B (solenoid valve) and the second canister is connected. The canister valve is left closed.

4.1.6 The ON button of timer #2 is pressed. The flow through the flow controller should be stopped by this action.

4.1.7 The flow controller switch is turned to "READ" and the zero flow reading is obtained. If this reading is not stable, wait until the reading is stabilized.

4.1.8 The flow controller switch is turned to "SET" and the flow setting is adjusted to the algebraic SUM of the most recent entry on Table C-1 and the zero reading obtained in step 4.1.7 (If the zero reading is negative, SUBTRACT the zero reading from the Table C-1 value). Be sure to use the correct Table C-1 flow value for one or two canisters, as appropriate. [Note: If the analytical laboratory determines that the canister sample pressure is too low or too high, a new flow setting or settings will be issued for the sampler. The new flow setting should be recorded in Table C-1 and used until superseded by new settings.]

4.1.9 Timer #2 is turned OFF to again start the flow through the flow controller. With the pump (timer #1) ON and the sampling valve (timer #2) OFF, the flow controller is turned to "READ" and the flow is verified to be the same as the flow setting made in step 4.1.8. If not, the flow setting is rechecked in step 4.1.8 and the flow setting is readjusted if necessary.

4.1.10 The OFF button of timer #1 is pressed to stop the pump.

4.1.11 The canister valve(s) are fully opened.

4.2 Timers

4.2.1 Timer #2 is set to turn ON at the scheduled ON time for the sample period, and OFF at the scheduled OFF time. (See the subsequent section on setting the timers.)
Normal ON time: 12:00 AM on the scheduled sampling day.
Normal OFF time: 11:59 PM on the scheduled sampling day.

(The OFF time is 11:59 PM instead of 12:00 AM so that the day number for the OFF time is the same as the day number for the ON time.) Be sure to set the correct day number.

4.2.2 Timer #1 is set to turn ON six (6) hours before the beginning of the scheduled sample period and OFF at the scheduled OFF time for the sample period (same OFF time as for timer #2). (See the subsequent section on setting the timers.) Normal ON time: 06:00 PM on the day prior to the scheduled sampling day. Normal OFF time: 11:59 PM on the scheduled sampling day. [Note: The timers are wired so that the pump will be on whenever either timer is on. Thus the pump will run if timer #2 is ON even if timer #1 is OFF.]

4.2.3 The elapsed time meter is set to 0.

4.3 Sampler Check

4.3.1 The following must be verified before leaving the sampling site:

(1) Canister(s) is (are) connected properly and the unused connection is capped if only one canister is used.
(2) Canister valve(s) is (are) opened.
(3) Both timers are programmed correctly for the scheduled sample period.
(4) Both timers are set to "AUTO".
(5) Both timers are initially OFF.
(6) Both timers are set to the correct current time of day and day number.
(7) Elasped time meter is set to 0.

4.4 Sampler Recovery (Post Sampling)

4.4.1 The valve on the canister is closed.

4.4.2 The canister is disconnected from the sampler, the sample data sheet is completed, and the canister is prepared for shipment to the analytical laboratory.

4.4.3 If two canisters were sampled, step 2.4.2 is repeated for the other canister.

5. Timer Setting

Since the timers are 7-day timers, the days of the week are numbered from 1 to 7. The assignment of day numbers to days of the week is indicated on the timer keypad: 1 = Sunday, 2 = Monday, 3 = Tuesday, 4 = Wednesday, 5 = Thursday, 6 = Friday, and 7 = Saturday. This programming is quite simple, but some timers may malfunction or operate erratically if not programmed exactly right. To assure correct operation, the timers should be reset and completely reprogrammed "from scratch" for each sample. The correct current time of day is re-entered to reprogram the timer. Any program in the timer's memory is erased by resetting the timer (pressing the reset button). The timer is set by the following:

(1) pressing the reset button,
(2) entering the correct day number and time of day,
(3) entering the ON and OFF times for the sample period, and
(4) verifying that the ON and OFF time settings are correct.

5.1 Timer Reset

The timer reset button is pressed, which is recessed in a small hole located just above the LED (light emitting diode) indicator light. A small object that will fit through the hole, such as a pencil, match, or pen is used to press the timer. After reset, the timer display should show |1| |10:00|. [Note: The timers may operate erratically when the batteries are discharged, which happens when the sampler is unplugged or without power for several hours. When the sampler is again powered up, several hours may be required to recharge the batteries. To avoid discharging the batteries, the battery pack should be disconnected from the timer when the sampler is unplugged.]

5.2 Date and Time Entry

The selector switch is turned to SET and the number button corresponding to the day number is pressed. (For example, a "2" is pressed for Monday.) The current time of day is entered. (For example, if the time is 9:00 AM, 900 is pressed.) AM or PM is pressed as applicable. (Display should show |2| |'9:00| for 9:00 AM Monday.) [Note: ' indicates AM and indicates PM.] The CLOCK button is pressed. (Display should show |-| |--:--|) If an error is made, |E| |EE:EE| is shown on the display. The CLEAR button is pressed and the above steps are repeated. The selector switch is turned to AUTO or MAN to verify correct time setting.

5.3 ON and OFF Entry

The selector switch is turned to SET. The ON and OFF program is entered in the following order: day, number, time, AM or PM, ON or OFF. (Example: To turn ON at 12:00 AM on day 5 (Thursday); 5, 1200, AM, ON is entered). (Example: To turn OFF at 11:59 PM on day 5 (Thursday), 5, 11:59, PM, OFF is entered.) If the display indicates an error (|E| |EE:EE|), the timer is reset. The selector switch is turned to AUTO.

5.4 ON and OFF Verification

5.4.1 The selector switch is turned to REVIEW. The number of the scheduled sample day is pressed. ON is pressed. The display should show the time of the beginning of the sample period (for example, |5| |'12:00|). [' indicates AM.] ON is pressed again. The display should show |5| |--:--|, indicating no other ON times are programmed.

5.4.2 OFF is pressed. The display should show the time of the end of the sample period, (for example, |5| |, 11:59|). PM is indicated by the "," mark before the time. OFF is pressed again. The display should show |5| |--:--|, indicating no other OFF times are programmed. The selector is switched to AUTO. If anything is incorrect, the timer is reset and reprogrammed.

TABLE C-1

NET FLOW CONTROLLER SETTING

DATE	1 CANISTER	2 CANISTERS

U. S. GOVERNMENT PRINTING OFFICE 1980/640-163/00313

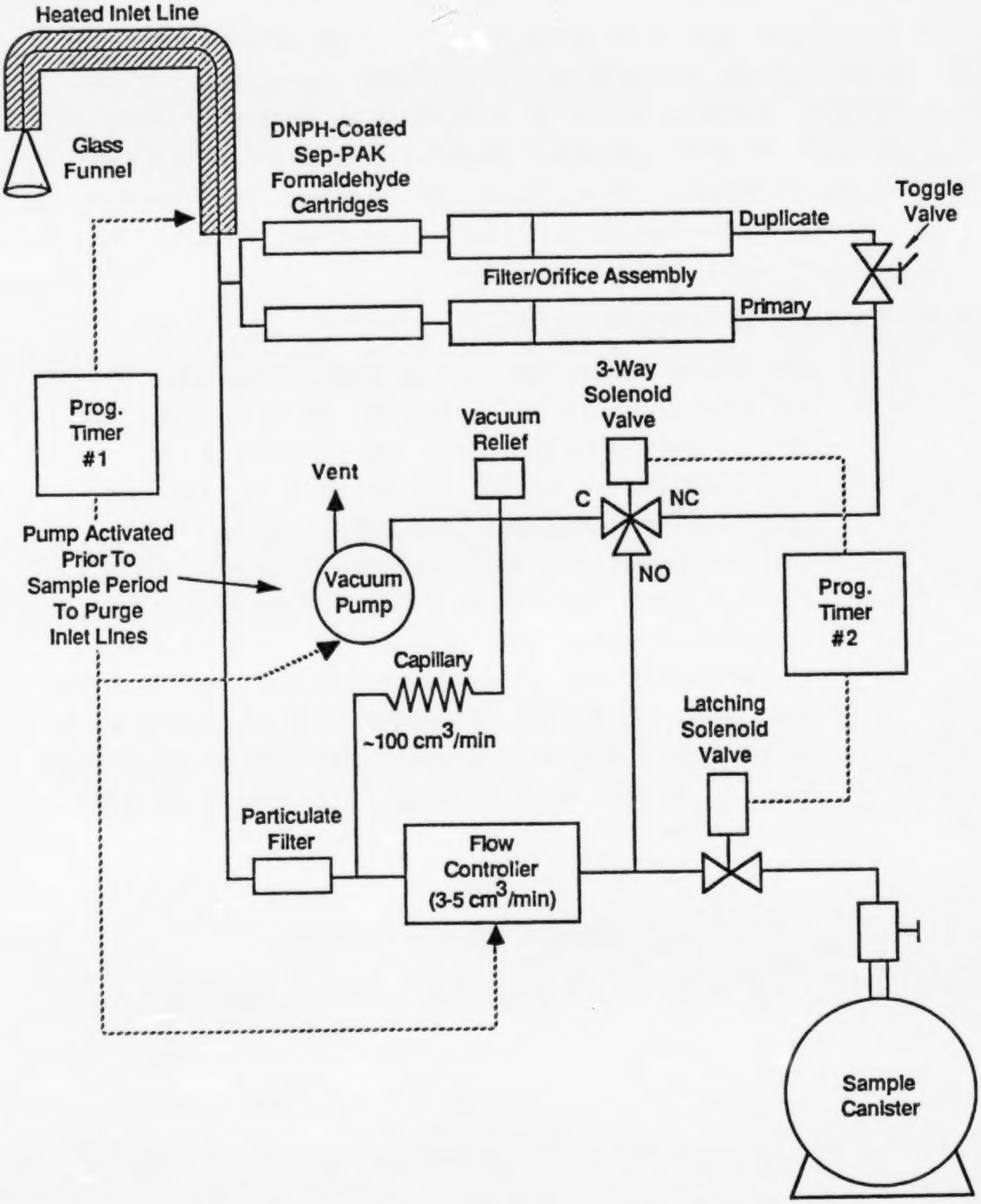

Heated Inlet Line
Glass Funnel
DNPH-Coated Sep-PAK Formaldehyde Cartridges
Duplicate
Toggle Valve
Filter/Orifice Assembly
Primary
Prog. Timer #1
3-Way Solenoid Valve
Vacuum Relief
Vent
C
NC
NO
Pump Activated Prior To Sample Period To Purge Inlet Lines
Vacuum Pump
Prog. Timer #2
Capillary
~100 cm3/min
Latching Solenoid Valve
Particulate Filter
Flow Controller (3-5 cm3/min)
Sample Canister

FIGURE C-1. U.S. ENVIRONMENTAL PROTECTION AGENCY UATP SAMPLER SCHEMATIC OF SAMPLE INLET CONNECTIONS